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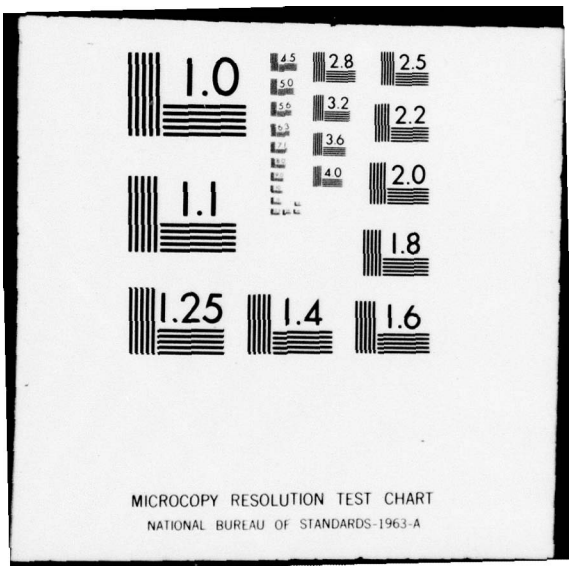
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ANNUAL TECHNICAL REPORT

MATERIALS RESEARCH LABORATORY

JULY 1, 1975 - JUNE 30, 1976

Brown University

Providence, Rhode Island 02912

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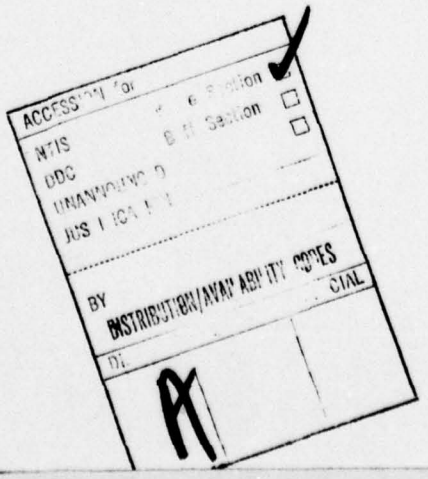

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PREFACE

The Materials Research Laboratory at Brown University is engaged in interdisciplinary research directed toward the solution of problems in various areas of Materials Science.

In this report, Section I - IV represent major thrust areas; the remaining sections are less extensive, since they cover either new areas of activity, emerging thrusts with a smaller number of investigators, or derive their principal funding from sources other than the NSF-MRL program.

Although the research summaries in this report are contributions from individual investigators, introductions to the four major thrust area summaries have been provided by investigators who during the reporting period assumed the functions of coordinators of that thrust area. These are: Microscopic and Macroscopic Dynamic Plasticity, R. J. Clifton; Fracture of Solids, J. R. Rice; Inorganic Glasses, W. M. Risen, Jr., and Chemisorption on Metallic Surfaces, P. J. Estrup.

Since many of the research areas are interrelated, cross references have been made when the work might with equal justice have been placed in two or more different sections.

The largest single source of support of this Laboratory is the Materials Science Branch of the National Science Foundation. Substantial support also came from thirteen other agencies, including the Office of Naval Research and, of course, Brown University.

The Materials Research Laboratory at Brown University is administered technically by a Director, Associate Director and a committee composed of faculty members in representative areas of materials science.

The present appointees are:

Director: G. S. Heller

Associate Director: C. Elbaum

Advisory Committee: R. H. Cole
L. N. Cooper
P. J. Estrup
J. R. Rice
J. Tauc

SECTION 1

INTRODUCTION

Microscopic and Macroscopic Dynamic Plasticity

Research in this area is directed towards understanding the mechanisms of plastic deformation. Projects in this area span investigations ranging from the study of dislocation mobility by means of ultrasonic attenuation experiments to the determination of the strain rate sensitivity of the flow stress by means of strain rate jump experiments. The overall effort includes plate-impact experiments, computer simulation of dislocation motion, x-ray topographic observation of dislocations and continuum descriptions of dislocation interactions.

Central to this research has been the stimulation of interaction among investigators with research interests in various aspects of dislocation phenomena. Computer simulation has been used to explore both the vibration of dislocations in ultrasonic attenuation experiments and the high speed motion of dislocations in plate impact experiments. On the other hand, ultrasonic attenuation methods have been developed to probe changes in dislocation configurations during strain-rate change experiments. Both the x-ray topographic studies and the continuum theory work on dislocation loops are expected to contribute to understanding of the glide bands observed in the plate impact experiments.

Major works completed during this period include the Ph.D. thesis by P. Kumar on dislocation motion and generation in LiF single crystals under plate-impact loading and the work on the effects of strain-rate and strain-rate history on the flow stress of four close-packed metals that is the Ph.D. thesis research of P. E. Senseny. A significant new development is the invention of an interferometer for monitoring both normal and transverse components of the motion of a plane surface. This interferometer is expected to be useful in plate-impact experiments designed to enhance the role of plastic deformation in determining the structure of the observed wave profiles. Such experiments, including pressure-shear loading due to impact of skewed plates and wave propagation in non-principal directions of single crystals, should contribute to improved understanding of the mechanisms of plastic deformation at high strain rates and dislocation velocities.

SECTION 1

Microscopic and Macroscopic Dynamic Plasticity

Individual Contributions

Dislocation Motion and Generation in LiF Single Crystals Subjected to Plate-Impact

A technique developed recently for subjecting a target to a single, approximately square pulse has been used to study dislocation generation and mobility in single crystals of LiF. The technique involves impact of a LiF crystal target by a thin ($\simeq$ 0.8mm), eight-pointed star, aluminum flyer plate. The target is backed by an aluminum plate that serves as a momentum trap and prevents reloading due to reflected longitudinal waves. The eight-pointed star flyer plate causes the unloading waves generated from the free edges to be reflected around the outside of the crystal in such a way that a central octagonal region is relatively unaffected by these unloading waves. Thus, in this central octagonal region the loading is essentially that of a single, plane pulse.

Experiments have been conducted in which pulses with duration of approximately 0.25 μsec and amplitudes corresponding to resolved shear stresses of 0.05 to 0.1 GPa have been propagated along <100> directions. Examination of dislocation structures by etch pit techniques reveals that dislocation density increases from approximately 5×10^4 cm^{-2} to 10^6 - 10^7 cm^{-2}. Many of the new dislocations are present in glide bands corresponding to slip on a single slip plane. Glide bands intersecting the front and rear surfaces are longer and more closely spaced than those in the interior. Continuing work is directed towards determining the structure of these glide bands and the mechanisms by which they are produced.

Principal Investigator: R. J. Clifton (Engineering)

Personnel: P. Kumar (Engineering), L. Hermann, (Engineering), and W. Rebello (Engineering)

Publications: Kumar, P., "An Investigation of Dislocation Motion and Generation in LiF Single Crystals Subjected to Plate-Impact," Ph.D. Thesis, Brown University, May 1976.

Clifton, R. J., "Some Recent Developments in Plate Impact Experiments," Propagation of Shock Waves in Solids (ed. by E. Varley), ASME, New York, 1976, pp.27-40.

Supported by the Materials Research Laboratory/NSF/ARPA, and the National Science Foundation.

Dislocation Dynamics

High-Speed Dislocations The phenomenon of breakdown in the regular motion of dislocations and subsequent dislocation multiplication in lattice models as they approach a relevant sound speed in the crystal has been described in previous technical reports. It has now been found by computer simulation that corresponding inertia effects are important when high-speed edge dislocations leave the free surface of a crystal and cause dislocation regeneration there. The existence of this multiplication mechanism was conjectured in 1948 by F. C. Frank.

Vibrating Dislocations The computer simulation of an atomistic model of a vibrating dislocation has been described in the previous technical report. The first version of this model included only that anharmonicity enforced by the periodicity of the crystal but was locally harmonic. The effects of additional local anharmonicity are now being studied.

Principal Investigator: J. H. Weiner (Engineering)

Personnel: A. Needleman (Engineering), Y. Y. Earmme (Engineering) and R. Hsu (Engineering)

Publications: None

Supported by the Materials Research Laboratory/NSF/ARPA.

Ultrasonic Studies of Strain Rate Effects in the Deformation of Solids

We have reported earlier the development of a method to study changes in ultrasonic wave propagation (changes in attenuation and in velocity) assocated with short duration, high amplitude stress pulses. The purpose of this approach is to study, in real time, the effects of high stresses and high strain rates, as well as of rapid increases in strain rate, on the behavior of dislocations. The technique in question has been perfected to the point that a series of experiments has been carried out on aluminum single crystals subjected to stress pulses less than 100 microseconds in duration. Studies of dislocation properties as a function of prior strain history are being undertaken.

Principal Investigator: C. Elbaum (Physics and Applied Mathematics)

Personnel: A. Hikata (Applied Mathematics)

Publications: None

Supported by the Materials Research Laboratory/NSF.

Dynamic Properties of Structural Materials

This research project is concerned with the inelastic behavior of structural metals as it is affected by the rate of deformation or the rate of loading and involves experiments in dynamic plasticity and dynamic fracture initiation. An important goal is the development of constitutive equations for material behavior that include the effects of the history of strain rate as well as the current values of strain and strain rate and also includes temperature. In dynamic fracture our goal is to study fracture initiation mechanisms as they are influenced by the rate of loading (more precisely, by the time elapsed from first loading of the fracture site to fracture initiation). We plan to conduct experiments on various metals (steels and structural aluminum), and at different temperatures. We also plan to study the role of inclusions on fracture initiation. We shall also relate the dynamic plasticity properties to those of dynamic fracture initiation.

The dynamic plasticity experiment utilizes the classical Kolsky (split-Hopkinson bar) technique, but adapted for torsional or shear loading of the specimen. Dynamic loading pulses are initiated either by an explosive detonation or by the sudden release of stored torque. The explosive loading technique offers a rise-time of about 7 microseconds in the incident pulse so that the strain rate at which the specimen is deformed goes from zero to its maximum value within that time. The pulse has a duration of about 50 microseconds during which the strain rate remains constant. The stored torque apparatus offers a longer loading pulse, 500 microseconds, resulting in greater specimen strain, but with a rise-time of about 40 microseconds. Incremental strain rate experiments can be performed with either the stored-torque or the explosive facility. In an increment test the specimen is loaded first at a quasi-static strain rate of about 10^{-4} s^{-1} to some pre-selected strain whereupon a dynamic strain rate of order 10^{3} s^{-1} is superimposed. This technique provides an excellent tool for separating strain rate effects from strain rate history effects for the material being studied. Experiments of this type have been performed with specimens at temperatures ranging from -200C to 250C. Tests at temperature employ tapered Kolsky bars which preserve constant mechanical impedance along their length in spite of temperature gradients on each side of the heated or cooled specimen. Incremental strain rate experiments have been performed on 1100-0 aluminum, OFHC copper, zinc and a magnesium alloy over this range of temperature.

The dynamic fracture experiment is also based on an adaptation of the Kolsky bar. The specimen is a 1-inch diameter notched bar which is first fatigued in a special apparatus to produce a circumferential fatigue crack at the root of the notch. An explosive detonation at one end of the fatigued specimen produces a tensile loading pulse which fractures the specimen within 20-25 microseconds after its arrival at the notch site while the loading pulse is still increasing in amplitude. The portion of the loading pulse that is transmitted through the notched area is measured by strain gages and is interpreted as a measure of the average stress at the fracture site as a function of time. Crack opening displacement is also monitored and recorded as a function of time using an optical extensometer system which bridges the notch.

This technique shows great promise and has been successfully applied in room temperature experiments on 1018 cold rolled steel (nominally ductile) and 4340 hardened and tempered tool steel (nominally brittle). The advantage this technique has over previous methods lies in its loading rate, about 500 times faster than previously reported, and in its unambiguous measures of stress and crack opening displacement as functions of time.

Principal Investigator: J. Duffy (Engineering)

Personnel: R. H. Hawley (Engineering), P. E. Senseny (Engineering), L. S. Costin (Engineering), P. Rush (Engineering) and G. J. LaBonte (Engineering).

Publications: Senseny, P. E., Duffy, J., and Hawley, R. H., "The Effect of Strain Rate and Strain Rate History on the Flow Stress of Four Close Packed Metals," Brown University Technical Report in preparation.

Costin, L. S., Duffy, J., and Freund, L. B., "Fracture Initiation in Metals Under Stress Wave Loading Conditions," Presented at ASTM Symposium on Fast Fracture and Crack Arrest, June 1976, Chicago, Illinois. To be published in ASTM special technical publication.

Supported by the Materials Research Laboratory/NSF/ARPA, and the United States Army (ARO-Durham)

Studies in the Continuum Theory of Dislocations

The early part of this study was directed at an increased understanding of the "integral theory" for dislocations in linear anisotropic elastic media, and especially in relating it to the "geometrical" constructions used for computing the elastic strain and stress fields of complex arrays of dislocations and dislocation loops. Following up on earlier work in this area, we have been able to reduce the problem of determining the elastic field of an arbitrary dislocation loop to that of evaluating the field of an infinitely extended (i.e. straight) dislocation. The resulting procedures yield formulae that are considerably easier to apply, in certain cases, than those previously proposed in the literature. Specific applications have been made to planar problems such as the determination of equilibrium shapes of dislocation networks and to dislocation "self-force" computations. Other applications include studies of the interaction of dislocations with cracks and second phase particles. These latter studies are of considerable

interest in relation to our studies of microscopic mechanisms in fracture and metal plasticity including dislocation generating mechanisms in dynamic plasticity.

Principal Investigator: R. J. Asaro (Engineering)

Personnel: None

Publications: Asaro, R.J., "Comments on the Geometrical Theorems for Dislocations in Anisotropic Elastic Media," Brown University Report 94, October 1976.

Asaro, R. J. and Barnett, D.M., "Applications of the Geometrical Theorems for Dislocations in Anisotropic Elastic Media," published in Conference on Computer Simulation for Materials Applications, April, 1976, Gaithersburg, MA.

Supported by the National Science Foundation and the Materials Research Laboratory/NSF.

Computer Simulation of Segmented Slip

This research project is concerned with the computer simulation of dislocations many through a field of randomly dispersed point defects. These point defects themselves have a random dispersion of attractive and repulsive strengths relative to the dislocations. The array of defects is then read by the computer and a dislocation is made to pass through this field until it makes contact with the obstacles. The dislocation bows out between obstacles and eventually tears away from the attractive obstacles. By varying the velocity of the dislocation line, the velocity dependence of the interaction between the defects and the dislocation was observed in an interactive fashion and recorded on motion picture film. These films show indications of breakdown of either the dislocations or the model as dislocation speeds approach one-tenth the speed of sound.

Principal Investigator: M. H. Richman (Engineering)

Personnel: S. C. Danforth (Engineering) and T. Stryker (Computer Programmer)

Publications: None

Supported by the National Science Foundation.

X-Ray Topographic Techniques and Applications

Techniques Analysis of the x-ray topographic techniques based on our previous development of a treatment of the geometrical effects inherent in x-ray topography has continued. In particular, a stereographic projection method has been developed which allows one to incorporate the dynamical theory geometrical analysis into the design and interpretation of anomalous transmission experiments. The stereographic projection method is a scheme to display the results of elaborate computer calculations in a graphical way that allows one to see how various factors of the dynamical theory description of the diffraction process, such as geometrical divergence, x-ray source size, etc., affect the dislocations image quality and its characteristics. Because of the large number of experimentally variable parameters which must be considered, the computed data is very difficult to synthesize and to grasp in its entirety. This graphical development allows one to "see how it all fits together" in a semiquantitative fashion and, hence is important in both design and interpretation of x-ray topographic data. For example, the difficulties in assignment of Burgers vectors from diffraction contrast experiments which can occur purely as a result of the geometric features of the experiment can be quickly assessed and, thus, avoided; and the control of stereoscopic images for three dimensional viewing can be optimized. This work has been done in collaboration with C. Cm Wu and R. J. Armstrong of the University of Maryland and M. C. Narasimhan of Allied Chemical.

Microplastic Slip in Single Crystals

Microplastic slip observations employing combined etch pit and x-ray topographic obeservations of dislocation propagation in single crystals of Fe 3 percent Si are continuing. Slip initiation and propagation on a single (112) slip plane in a crystal loaded in three point bending indicate that both the initiation stress for dislocation source activation and the dislocation velocity are asymmetric, in the sense that a lower initiation stress and a larger velocity are observed for slip in the "easy" ⟨111⟩ direction than in the opposite direction. Computer calculations of the Schmid factor on all possible slip systems of both {112} and {110} types suggest that an asymmetry should also be expected in the workhardening characteristics for crystals having single (112) slip orientations and that this must be considered in microscopic slip asymmetry studies.

Principal Investigator: B. Roessler (Engineering)

Personnel: W. Oates (Engineering)

Publications: Narasimhan, M. C. and Roessler, B., "Stereoscopic Imaging of Dislocations by Anomalous Transmission X-Ray Topography," Microstructural Sicence, 3, (1975) p. 583.

Supported by the National Science Foundation and the Materials Research Laboratory/NSF.

Pressure-Shear Waves

A new interferometer has been developed for monitoring both normal and transverse components of the motion of a plane surface. This interferometer makes use of the reflected beam and two symmetrically diffracted beams arising from illumination of a diffraction grating by a laser beam at normal incidence. Experiments have been conducted with a 200 lines/mm grating copied onto a plane surface by means of a photo-resist technique. The normal motion is monitored by means of a standard Michelson interferometer in which the zeroth order diffracted beam corresponds to the beam reflected from a moving mirror. The transverse motion is obtained by combining +nth and -nth order diffracted beams and monitoring the intensity of the composite beam. The transverse displacement interferometer (TDI) is insensitive to normal motion and has a sensitivity to transverse motion of (d/2n) per fringe where d is the pitch of the grating and n is the order of the diffracted beams employed. The new interferometer has been used for monitoring the motion of the rear surface of a Y-cut quartz plate due to impact by a similar plate. The TDI employed the two fourth order diffracted beams, with a resulting sensitivity of 0.625 μm per fringe. The recorded motion exhibits the predicted features of two coupled elastic waves, each involving both normal and transverse motion. Quantitative agreement between theory and experiment is within the error that is attributed to tilt between target and flyer plates. Overall, the interferometer works well and should be useful for studying elastic-plastic waves due to combined pressure-shear loading as well as for other applications where measurements of combined normal and transverse displacements are required.

Principal Investigator: R. J. Clifton (Engineering)

Personnel: K. S. Kim (Engineering) and L. Hermann (Engineering)

Publications: Abou-Sayed, A. S., and Clifton, R. J., "Pressure Shear Waves in Fused Silica," J. Appl. Phys. 47, 1976, pp. 1762-1770.

Abou-Sayed, A. S., and Clifton, R. J., "Pressure-Shear Waves in 6061-T6 Aluminum Subjected to Oblique-Plate Impact," (to appear in J. Appl. Mech.)

Abou - Sayed, A. S. and Clifton, R. J., "Analysis of Pressure-Shear Waves in an Elastic/Visco-Plastic Material," (to appear in J. Appl. Mech.)

Supported by the Materials Research Laboratory/NSF/ARPA, and the National Science Foundation.

SECTION 2

INTRODUCTION

Fracture of Solids

Studies on the fracture of solids continue to emphasize the relation of microstructure and microstural rupture processes to macroscopic toughness. A number of the studies completed in the current reporting period relate to fracture processes at a macroscopic crack tip. The large-strain elastic-plastic finite-element program was applied by McMeeking and Rice to analyze the plastic opening at a crack tip under plane strain conditions. This has given a far more accurate description than previously available of the stress and strain fields in the near tip region where fracture nucleation occurs. The theoretical solutions allow investigation of path dependencies of the J integral on contours very close to the crack tip. They also serve together with our previous results on elastic-plastic stress analysis, as a starting point in relating microstructural fracture mechanisms to macroscopic toughness in various structural alloys. Work of this type includes the experimental studies of Gurland and Rawal on cleavage fracturing of spheroidized steels, and the analysis by McMeeking of ductile fracture of various steels and aluminum alloys, reported separately in the literature, in terms of hole nucleation and growth to coalescence. The results by Gurland and Rawal correlated well with the concept of a critical stress for cleavage nucleation, predicted in terms of carbide size and spacing by the Smith model.

Further work on microstructural fracture mechanicms includes a study begun by Gurland and Fisher on crack and cavity nucleation from carbide inclusions in spheroidized steel, and studies by Gurland, Lee and Pickens on the microstructural basis for strength and fracture toughness in cemented carbides (WC-Co).

In work on the continuum mechanical description of elastic-plastic crack growth, Kfouri and Rice developed an expression for energy releases in finite crack growth steps based on the Dugdale--Bilby-Cottrell-Swinden crack tip yielding model. They verify the theoretically anticipated limit of a vanishing energy surplus for continuous elastic-plastic crack growth, and also propose a basis for growth predictions based on a finite growth step size, considered characteristic of the material. A major program of elastic-plastic finite element analysis for quasi-statically extending cracks was begun in this reporting period. Full solutions were carried out by

Sorensen for the anti-plane strain case, since there is a relatively complete theoretical development for that case by McClintock and others. The numerical results were found to correspond closely to the theoretical solutions, given the usual mesh-size uncertainties, and the numerical techniques are considered reliable for analysis of the more interesting plane strain case.

In the area of dynamic crack propagation, Freund has concentrated on the use of numerical and other approximate methods in the dynamic analysis of crack propagation in structural elements. This has included a study of crack propagation across a section of a flexurally loaded beam and, in work with Abou-Sayed, a study of the dynamics crack propagation in a gas pressurized pipeline. Also, Freund and Burgers began the development of a general numerical analysis program for two-dimensional elasto-dynamic problems of unsteady crack motion. The elasticity equations are written by finite differences in characteristic form along the bi-characteristic directions. In related experimental studies, Kolsky and Kinra have completed high-speed photgraphic and strain-guage measurements of waves emitted in dynamic crack propagation across glass and brittle plastic rods subjected to tensile and bending loads.

Asaro, Needleman and Rice have investigated various aspects of the localization of plastic flow into shear bands, or into local necks in sheet materials, as a precursor to ductile rupture. One aspect under study by Asaro and Rice concerns shear localization into coarse slip bands in the deformation of ductile single crystals. The work pursues the theoretical basis, in terms of non-Schmid stress effects on the criterion for slip, of the experimental association between the onset of cross-slip and shear localization in fcc crystals. The studies by Needleman on local necking in biaxially stretched sheets have the aim of resolving the paradoxial prediction of essentially unlimited ductility, according to classical isotropically hardening plasticity models. The factors considered include the role of small initial non-uniformities in sheet thickness and also the effect of vertex-like models for subsequent plastic yield surfaces. Both lead to significant ductility reductions.

Further studies have been directed to the process of shear faulting and fault propagation in geological materials. For example, Rice, Simons, and Cleary have developed solutions for shear fault propagation in a Biot fluid infiltrated elastic solid and shown that the coupling between deformation and fluid diffusion serves to stabilize the fault against rapid propagation, giving a possible basis for observed creep-like propagations of slip events along faults. Also, Rudnicki has modelled the instability process in a rock mass containing a local non-linear strain-weakening zone

in the form of an ellipsoidal inclusion, subjected to steadily increasing remote stress.

In othere studies, Beevers has examined crack closure effects in fatigue crack propagation, and Mason and Rice have begun a study of factors controlling brittle versus ductile response of grain boundaries containing atomistic segregations of impurities with special reference to data of Hondros and MacLeanon on the embrittlement of Cu polycrystals by Bi.

SECTION 2

Fracture of Solids

Individual Contributions

Microscale Fracture Mechanisms

An experimental program has been started to study crack formation at inclusions and particles during the early stages of fracture. The current work attempts to elucidate the conditions of crack initiation at Fe_3C particles by the interfacial separation or particle cracking in steels. The controlled variables are (i) the composition of the steels, namely carbon content in the range 0.1 to 1.05% C, (ii) the state of stress, i.e. uniaxial in smooth specimens or triaxial in notched geometries, and, (iii) the temperature, in the range -196° to 20°C. The techniques of microscopic observation include optical microscopy of sections through the deformed specimen, scanning electron microscopy of fracture surfaces, and eventually transmission electron microscopy of thin sections. Interesting preliminary results are that particle fracture is a much more common occurrence than interfacial separation when the particles are dispersed, but that interfacial void formation is often associated with the matrix film between clustered particles.

A further study of the effect of cementite particles on the fracture toughness of spheroidized carbon steels at low temperatures is based on the results of S. Rawal and J. Gurland (previous report) and is specifically concerned with the size of the highly stressed region at the crack tip in which unstable cleavage fracture is nucleated and propagated. Richie, Knott and Rice (RKR) stipulate a region of 1-2 grains in which a critical cleavage stress is achieved. By matching the experimental K_{IC} values of our steels with the RKR procedure, we obtain an average size of 1.3 grains. Our results support the RKR model for cleavage fracture and suggest that the critical event includes the propagation of the crack through a grain boundary, thereby requiring the highly stressed region to be larger than one grain. Good agreement was obtained between measured K_{IC} values and those calculated by the RKR procedure not only under linear elastic stress conditions but also for small scale yielding

conditions (with plastic-elastic stress ditribution) provided that the mode of fracture initiation is by cleavage, as, for example, in steels of high carbon content and at low temperatures.

Principal Investigator: J. Gurland (Engineering)

Personnel: J. Fisher (Engineering), S. Rawal (N.E. Metals Co., Manville, RI) and H. Stanton (Engineering)

Publications: Rawal, S.P., Gurland, J., "Observations on the Effect of Cementite Particles on the Fracture Toughness of Spheroidized Carbon Steels," Proc. 2nd Int. Conf. on Mechanical Behavior of Materials, ASM, Metals Park, Ohio (1976) pp. 1154-1158.

Supported by the United States Energy Research and Development Administration.

Hardness and Fracture Strength of Cemented Carbides

This study of the relation between the microstructure of cemented carbides, WC-Co, and their hardness and fracture toughness is in progress.

An attempt was made to predict the hardness of cemented carbides over the entire range of composition by combining the concepts of dispersion hardening and carbide skeleton deformation. We propose that the load carried by the alloy is the sum of the loads carried by the continuous carbide volume, and by the binder phase and that carbide volume not included in the skeleton, such that

$$H_V = V_C \, H_{WC} + (1 - V_C) \, H_m \qquad [1]$$

where V_C is the volume fraction of the continuous carbide volume, H_{WC} is the hardness of the carbide phase, and H_m is the hardness of the binder phase.

The volume fraction of the connected carbide volume, V_C, is not necessarily equal to the volume fraction of the carbide constituent, V_{WC}, and it can be shown that

$$V_C = C \, V_{WC} \qquad [2]$$

where C is the contiguity, i.e., the ratio of the area of carbide-carbide contacts to the total surface area of the carbide phase. Eq. 2 can now be rewritten as:

$$H_V = C \, V_{WC} \, H_{WC} + (1 - C \, V_{WC}) \, H_m \qquad [3]$$

The hardness of the binder phase, H_m, obeys a Hall-Petch function, obtained from the data of Dawihl and Frisch, namely;

$$H_m = 300 + 13.0\ \lambda^{-\frac{1}{2}}\ kg/mm^2 \qquad [4]$$

For the purpose of fracture toughness determination, the single edge notched beam (SENB) specimen was selected for reason of simple shape, low cost of manufacture and simple test procedure in three - point bending. The main effort during this period was devoted (a) to develop a technique of pre-cracking, and (b) to justify the fracture mechanics of the notch and crack configuration.

(a) Precracking: A successful means of precracking was achieved by electron discharge machining (EDM) with a thin copper foil. The normal low voltage EDM cutting is terminated by a brief high voltage discharge. This "zap" introduces thermal cracks at the root of the EDM notch.

(b) Fracture mechanics: In this work a root radius of 0.0006" is obtained, with small microcracks emanating therefrom. On the basis of the stress distribution ahead of a notch with finite radius and a crack of subcritical radius, a correction factor for K_{IC} was derived which accounts for the fact that an EDM notch coupled with small "natural" cracks is not necessarily identical to a "natural" crack of the same length. The correction factor is a function of root radius, ρ, microcrack length, b.

Principal Investigator: J. Gurland (Engineering)

Personnel" H.C. Lee (Engineering), J. Pickens (Engineering) and H. Stanton (Engineering).

Publications:. Lee, H.C., Pickens, J., and Gurland, J., "On the Hardness and Fracture Strength of Cemented Carbides," Proceedings of Vth Annual NSF Hard Materials Workshop, J.J. Mills, editor, Martin Marietta Laboratories, Baltimore, Maryland, (1976), pp. 61-68.

Supported by the National Science Foundation, Division of Materials Research, Metallurgy and Ceramics Section.

Dynamic Crack Propagation

Research has continued in the general area of dynamic crack propagation, with emphasis on the fracture of structural elements and the use of numerical or other approximate methods in the analysis of dynamic crack propagation. One project has concentrated on the dynamic fracture of beams subjected to bending or transverse loading. In previous work, an analysis was presented by means of which the length of a crack growing across a section of a beam and the bending moment at the fracturing section were determined as functions of time. The model predicted that the crack tip accelerates very quickly after initiation to a speed near the terminal speed for the material, travels at this speed through most of the beam thickness, and then rapidly decelerates in the final stage of the process. The main discrepancy between this prediction and experimental results is that the deceleration phase seems to begin earlier in the process than predicted. In an effort to resolve this discrepancy, the model is being modified to include the compressive stress on the fracturing section which is dynamically induced during the fracture process due to inertial resistance of the crack faces against separation.

A second problem area which has been investigated is that of crack propagation in an initially pressurized pipeline. In this study the pipe is modeled as an elastic or rigid-plastic thin shell and the gas is modeled as an ideal compressible fluid. Progress has been made toward understanding the role of backfill in retarding crack propagation in a buried pipeline and in modeling gas flow along the pipe and outflow through the opening crack.

A study has been initiated on the use of numerical methods in the analysis of dynamic elastic crack propagation. The numerical procedure is based on a second-order accurate finite-difference approximation of the equations of dynamic elasticity written in characteristics form along bicharacteristic directions. In the vicinity of the crack tip, where the elastic field is rapidly varying, the numerical solution is matched with the analytical description of the crack tip stress field which has been studied in detail in our previous work on crack propagation at nonuniform rates. The main objective of this work is the analysis of crack propagation in standard laboratory specimens, e.g., double cantilever beam or single edge-notched plate, and in structural elements.

Principal Investigator: L. B. Freund (Engineering)

Personnel: I. S. Abou-Sayed (Engineering) and P. Burgers (Engineering)

Publications: Freund, L. B., "Dynamic Crack Propagation," in The Mechanics of Fracture, Edited by F. Erdogan, ASME, New York, 1976.

Hermann, G., and Freund, L. B., "The Dynamic Fracture of Beams," 14th International Congress on Theoretical and Applied Mechanics, Delft, 1976.

Supported by the National Science Foundation and the Materials Research Laboratory/ARPA.

Macro and Micro-mechanics of Crack Growth in Ductile Structural Metals

A major program of finite element analysis has been completed on modelling the large plastic deformations that occur in the ductile opening of a crack tip under plane strain conditons. The analysis was based on the large-strain elastic-plastic finite element program developed by McMeeking and Rice, and numerical results obtained earlier in this study, based on conventional "small strain" elastic-plastic analyses by Tracey and Parks, were used to set outer-field boundary conditions for the finite deformation analysis of a small cut-out near the crack tip. The results are generally supportive of less precise earlier studies based on slip-line theory and have been used as a basis for assessing near-crack tip triaxial stress and strain levels and path-dependence of the J integral, and for carrying out studies of ductile hole growth for cavities which are nucleated at various angles relative to the crack tip.

The studies of the J integral suggest that it is essentially path-independent well into the plastic zone, except on contours of radius (in the undeformed state) which are approximately 4 or less times the crack tip opening displacement, Thus the interpretation given earlier to J as a characterizing parameter for outer field, impressed upon the crack tip fracture zone, is verified, but the results also indicate that any applications of J based on an assumed path independence within the zone immediately adjacent to the blunting crack tip are suspect.

The predictions of conditions for the onset of crack growth, based on the growth to coalescence with the crack tip of a hole placed initially at a distance equal to an average void-site spacing, have been compared against

data from plane-strain fracture tests of a wide variety of steels and aluminum alloys. In general, predictions of the crack tip opening displacement at the onset of crack growth have the same trend as experimental results, when plotted as a function of the ratio of initial hole size to hole spacing, but the experimental results are typically over-predicted by 50% to 100% and there are significant uncertainties in choosing representative spacings for the model in relation to the actual statistics of void-site distributions. Also, the toughness is overpredicted by very large factors when the hole growth process is terminated early by an unstable shear band localization, and the toughness is, in general, underpredicted when the particles responsible for ductile rupture, such as spheroidized carbides in steel, require very large stresses or strains for hole nucleation.

The onset of crack growth in the more ductile structural metals is seldom coincident with a terminal, running crack instability. Rather, the fracture instability is usually preceded by a period of stable crack growth under rising load, and recent finite element studies have been directed to two aspects of this process. First, an examination has been given of a generalization of the Griffith energy balance approach to crack growth. In this, the crack grows in finite steps Δa, and the work per unit area absorbed over the fracture step Δa, as the tractions acting there are reduced proportionally to zero, is identified as an energy release G^{Δ}. It was shown from the numerical results that G^{Δ}/G, where G is the nominal elastic energy release rate, is unity when Δa is large by comparison to the plastic zone but that, in accord with a general theorem for elastic-plastic materials of bounded flow strength, the ratio seems numerically to approach zero as $\Delta a \to 0$. Fracture predictions based on a materially dependent Δa and critical G^{Δ} are found to involve initially stable growth for sufficiently large values of the ductility parameter $EG^{\Delta}/Y^2\Delta a$ (where E = elastic modulus and Y = flow strength).

A longer range program of finite element analysis has the goal of obtaining, for quasi-statically growing cracks, descriptions of the near tip elastic-plastic field of accuracy comparable to that which is available from our earlier work on the monotonically loaded, stationary crack. Such results should have application to the modelling of stress corrosion cracking as well as to crack growth under rising load. Thus far, the computing procedures have been carried out only for anti-plane shear, since there are a variety of exact analyses against which the growing crack procedures can be tested in that case.

In coordination with the theoretical studies, some work has been done on the experimental observation of crack tips at various stages of the process of growth from a fatigue pre-crack. The method involves propping open a loaded crack, by insertion of a split pin into a hole drilled along the crack line and additionally, by insertion of an epoxy filler into the crack space. The specimen, preserved in its state during crack growth, is then sectioned for observation of the near tip region. By combining these experiments with measurements, according to the technique developed by Paris and Hermann, of small changes in elastic compliance with crack growth, it is possible to stop loading programs for observation of the tip region at pre-selected amounts of crack growth.

Principal Investigator: J. R. Rice (Engineering)

Personnel: R. M. McMeeking (Engineering), E. P. Sorenson, (Engineering), L. Hermann (Engineering), A. P. Kfouri (Engineering).

Publications: McMeeking, R. M., "Finite Deformation Analysis of Crack Tip Openings in Elastic-Plastic Materials and Implications for Fracture Initiation," submitted to Journal of the Mechanics and Physics of Solids, 1976.

McMeeking, R. M., "Path Dependence of the J Integral and the Role of J as a Parameter Characterizing the Near Tip Field," presented at ASTM 10th National Symposium on Fracture Mechanics; in review for publication by ASTM in Symposium Proceedings.

Rice, J. R., "Elastic-Plastic Fracture Mechanics," in The Mechanics of Fracture (ed. F. Erdogan), Applied Mechanics Division (AMD) Volume, American Society of Mechanical Engineers, New York, 1976 (in press).

Kfouri, A. P. and Rice, J. R., "Elastic/Plastic Separation Energy Rate for Crack Advance in Finite Growth Steps," in Fracture 1977 (eds. D.M.R. Taplin et al.), Volume I, Solid Mechanics Division Publication, University of Waterloo, Canada (in press).

Supported by the United States Energy Research Development Administration and the Materials Research Laboratory/NSF/ARPA.

Localization of Plastic Flow

A feature common to several classes of ductile solids is that when deformed sufficiently into the plastic range, an essentially smooth and continuously varying deformation pattern gives way to highly localized plastic deformation

in the form of a "shear band". Often such bands are the site of profuse void nucleation and growth, so that the localization of flow is then a direct precursor to ductile fracture. The continuum mechanics of localization has been explored as a bifurcation point in a program of previously homogeneous plastic deformation, and specific calculations of critical conditions have been carried out for a variety of elastic-plastic material models. In general these include an assessment of the destabilizing role of non-normality, as well as of vertex-like yielding.

A case pursued in some detail is the modelling of shear localization into coarse slip bands in the single-shear of ductile crystals. Here theoretical results predict localization with a positive strain hardening modulus when stresses other than the Schmid resolved shear stress govern the criterion for continuing plastic flow. A specific case in which non-Schmid stresses are expected to be important is that of a crystal deforming with screw dislocation segments bypassing local obstacles by cross slip. Indeed, there seems in the experimental literature to be an association between localization and the onset of cross slip, and for this reason a study has been initiated on a dislocation model for stress state dependence of the cross-slip process; this has the goal of predicting from fundamental considerations the constitutive parameters which enter into the criterion derived for localization.

Some experiments have been initiated on metal alloy crystals which display extreme forms of localized plastic flow. The objectives of these studies are to attempt comparisons between observed and predicted critical strain hardening rates at localization and to study the mechanisms by which damage accumulates within the bands.

Additional studies have been initiated on the possible role of small initial non-uniformities of material properties, in leading to localization at smaller overall deformations than predicted by the bifurcation approach as applied to initially homogeneous materials. The effect is thought to be particularly important at deformation states well removed from plane strain (e.g., axially symmetric extension or compression) as these are strongly resistant to localization according to the bifurcation approach. The analysis is being carried out for a constitutive model of an isotropic, void-containing elastic-plastic material developed by Gurson, and the initial volume fraction of holes is taken to be slightly larger within a thin planar slice of material than within the solid generally.

Principal Investigators: J. R. Rice (Engineering) and
R. J. Asaro (Engineering).

Personnel: J. W. Rudnicki (Engineering), H. Yamamoto (Engineering)

Publications: Rice, J. R., "The Localization of Plastic Deformation," in Theoretical and Applied Mechanics (Proceedings of the 14th International Congress on Theoretical and Applied Mechanics, Delft, 1976, ed. W. T. Koiter), Vol. 1, North-Holland Publishing Co., 1976, pp. 207-220.

Supported by the United States Energy Research Development Administration and the Nippon Steel Corporation.

Fundamentals of Brittle versus Ductile Response of Grain Boundaries

Work initiated in the previous year of the study has attempted to define conditions which allow an interface between grains or phases to undergo an atomistically brittle interfacial separation. This has been pursued with specific reference to environmental effects, e.g., hydrogen embrittlement, with the understanding that energy alterations due to solute segregation along internal interfaces may be essential to allowing the stability against dislocation blunting of an otherwise unstable atomistically sharp crack tip configuration. Some of the ideas involved can be tested against experimental results in the case of Cu polycrystals containing small amounts of Bi in solid solution. The Bi segregates preferentially along grain boundaries and experimental observations by Hondros and MacLean have reported fracture ductilities as a function of grain boundary coverage up to a few monolayers. Our studies to date have attempted to determine the range of bi-crystalline orientations that are consistent with brittle response, as a function of the segregant concentration or of its equilibriating potential. The study is still underway

Principal Investigator: J. R. Rice (Engineering)

Personnel: D. Mason (Engineering)

Publications: None

Supported by the United States Energy Research Development Administration.

Mechanics of Shear Rupture in Fluid Infiltrated Porous Materials

This study is directed to the modelling of shear rupture processes in natural rock masses, with special attention to those processes for which mechanical interactions between a deforming rock mass and its pore-fluid are essential in determining the time scale of rupture.

A mathematical solution developed for a quasi-statically extending shear crack in an elastic porous medium leads to a speed-dependent stress concentration at the fault tip. This arises from the coupling with the consolidation/diffusion processes involving the pore fluid, and the effect is to stabilize the fault in the sense that, up to a critical stress level, an increasing stress is required to achieve an increasing (but still quasi-static) fault speed. The effect has been suggested as a contributory mechanism to observed creep events on earth faults.

Another group of studies is directed to modelling processes which occur prior to unstable rupture in the form of an earthquake. Thus far, the studies have addressed the modes of instability that are possible for a weakened inclusion, representing previously faulted material within a more coherent rock mass that is subjected to tectonic shearing. Conditions for localization and for "run-away"instabilities have been defined, and the continuing work is directed to an assessment of fluid coupling effects as a possible contributor to the time scale of earthquake precursor events.

Principal Investigator: J. R. Rice (Engineering)

Personnel: J. W. Rudnicki (Engineering), M. P. Cleary (Engineering), and D. A. Simons (Engineering).

Publications: Rice, J. R. and Simons, D. A., "The Stabilization of Spreading Shear Faults by Coupled Deformation-Diffusion Effects in Fluid-Infiltrated Porous Materials," Journal of Geophysical Research, Vol. 81, pp: 5322-5334, 1976.

Simons, D. A., "Boundary Layer Analysis of Propagating Mode II Cracks in Porous Elastic Media," submitted to Journal of the Mechanics and Physics of Solids, 1976.

Rudnicki, J. W., "The Inception of Faulting in a Rock Mass With a Weakened Zone," to be published in Journal of Geophysical Research, 1977.

Supported by the National Science Foundation/Geophysics Program.

Brittle Fracture of Solids

Work has continued on the stress waves generated by brittle fracture of rods of glass and of various brittle plastics, both in tension and in bending. The experimental techniques included high-speed cinematography both of the cracks and of the photoelastic fields produced by the dynamic stress field, as well as strain gage measurements of the stress pulses as they propagated through the specimens. A number of new features have been observed, in particular the effect of the viscoelastic response of the polymers on the fracture process. Thus polystyrene specimens behaved very similarly to glass ones, allowing for the difference in modulus, while specimens of polymethylmethacrylate (plexiglas) which has much the same elastic modulus as polystyrene responded very much more slowly in the flexural fracture tests. This has been attributed partly to the damping of stress waves by this material, so that the reflected tensile pulses from the ends of the specimen were attenuated before arriving at the fracture plane and partly to the fact that the strength of this material is very rate sensitive. The work has been described in the Ph.D. theses of Drs. Kinra and Shih as well as in the publications listed below.

Principal Investigator: H. Kolsky (Applied Mathematics)

Personnel: V. Kinra (Engineering), S. Shih (Engineering)
R. Stanton (Applied Mathematics)

Publications: Kolsky, H. and Kinra, V., "The Interaction between Bending Fractures and the Emitted Stress Waves,", J. Engrg. Fracture Mechanics (in press), 1977.

Kolsky, H., "Stress Pulses Emitted in the Brittle Fracture of Solids," ASME, The Mechanics of Fracture, 1976.

Supported by the Materials Research Laboratory/NSF/ARPA.

Critical Tests of Fracture Criteria

The purpose of the present tests is a study of fracture criteria suitable for fracture with substantial plastic zones, where the present methods of assessing fracture toughness appear incomplete or inadequate. A large number of tests have already been performed with round bar specimens with circumferential cracks made in specially constructed fatigue equipment ensuring a high concentricity. The final testing was in controlled central axial tension, with a monitored crack opening at four points around the circumferential cracks. The results with aluminum alloy and maraging steel bars were analysed and found to represent mostly "brittle" fractures, i.e. with net fracture stress significantly

lower than the flow limit. Studies were made of the size and mechanical properties of specimens which would cover the range up to clearly ductile fracture. In addition, a preliminary study was made of methods for performing fracture tests under high hydrostatic pressure.

Principal Investigator: C. Mylonas (Engineering)

Supported by the Materials Research Laboratory/ARPA.

Fatigue Behavior of Thick-Walled Tubes

Thick-walled tubes are subjected to cyclic high internal pressure until failure by fatigue. Fatigue strength under such conditions is only a fraction of that expected. Means of improvement are being investigated. In particular, the effect of autofrettage and various surface treatments are being explored. Doubling the fatigue strength caused multiple testing machine failures, which are being corrected.

Principal Investigator: W. N. Findley (Engineering)

Personnel: R. M. Reed (Engineering)

Publications: None

Supported by the Union Carbide Corporation, Chemicals and Plastics.

Local Necking in Thin Sheets

When a ductile metal sheet is deformed in biaxial tension, as occurs in many sheet metal forming operations, it is generally observed that the sheet fails by a process of strain localization in a narrow neck. Such localized necking plays an important role in limiting the achievable ductility in sheet metal forming operations. However, when an initially uniform sheet subject to biaxial tension is analyzed within the framework of the classical smooth yield surface theory of a rigid plastic solid, unlimited ductility is predicted. The limited ductility of such sheets has been accounted for within the framework of classical plasticity theory by assuming the presence of an initial thickness inhomogeneity, although experiments showed that the thickness inhomogeneities needed to account for the experimental results were much longer than

those present in the test specimens. Alternatively, Stören and Rice showed that a theoretical analysis that models vertex-like yielding effects predicts finite ductility even for an initially uniform sheet. An analysis of necking in a curved sheet, assumed for simplicity to be in the shape of a spherical membrane, was carried out in order to investigate: i) the effect of sheet curvature on both diffuse and localized necking; ii) the effect of material as well as thickness homogeneities on the predictions of the classical theory of plasticity, and iii) the effect of inhomogeneities on localized necking when vertex-like yielding effects are taken into account. This investigation revealed that the curvature of the sheet had no direct effect on the development of a localized neck. However, at least for the specific case studied, diffuse necking modes became available prior to the localized mode. Thus, there is the possibility that in a curved sheet, the nonlinear interaction between the diffuse and localized modes may significantly affect the development of a localized neck. It is anticipated that such interaction effects will be the subject of future work. It was also found that small, localized variations of material properties could bring the local necking predictions of the classical plasticity theory more nearly in accord with experimental results, at least for the particular case studied of equal biaxial tension.

Furthermore, small inhomogeneities were found to significantly lower the strain required for local necking according to the vertex-like yielding model. With the same small inperfection level, this vertex model predicts that the onset of localized necking will occur at lower strain levels than does the classical theory. The above and other analyses of local necking in thin sheets were carried out within the framework of the two dimensional theory of plane stress, even though such necking is inherently a three-dimensional phenomena. Therefore, an investigation was undertaken, in collaboration with Dr. V. Tvergaard of the Technical University of Denmark, of the influence of three dimensional effects on the process of strain localization. Both analytical studies of the bifurcation problem governing the onset of necking and numerical finite element studies of the development of a neck were carried out. For simplicity, the particular problem of a biaxially stretched circular plate was considered. In most cases, reasonable qualitative agreement was found between the three dimensional and plane stress analyses, although three dimensional effects delayed the onset of necking somewhat. However, for a high hardening material, it was found that for the particular plasticity theory employed to model vertex-like effects, necking modes not accounted for by a plane stress analysis played a role in limiting ductility.

Principal Investigator: A. Needleman (Engineering)

Personnel: None

Publications: Needleman, A., "Necking of Pressurized Spherical Membranes," J. Mech. Phys. Solids - in press.

Needleman, A., and Tvergaard, V., "Necking of Biaxially Stretched Elastic-Plastic Circular Plates," DCAMM Report No. 116.

Supported by the Materials Research Laboratory/NSF.

Fatigue in Titanium

The fatigue crack growth behaviour of α-titanium in the range ΔK (threshold) to $\sim$ 20 MN $m^{-3/2}$ was studied using modified 25 mm thick compact tension specimens. The specimens were vacuum annealed at 700°C prior to testing. The crack length monitored by changes in specimen compliance to an accuracy of $\sim$ 0.05 mm.

The crack growth data showed that ΔK (threshold) levels of 2 MN $m^{-3/2}$ for $R \simeq 0.7$ could be achieved. The test procedure also allowed an estimate to be made of the value of K_o, the stress intensity to obtain a fully opened crack and hence a measure of the extent of "crack closure". The results showed that "crack closure" occurred during the extension of cracks by cyclic loading when the K level was less than 10-12 MN $m^{-3/2}$ and hence under effective plane strain conditions. The threshold levels could not be directly attributable to crack closure. There was some degree of scatter in the results but ln. $(K_{max} - K_o)$ v ln da/dN gave an improved presentation of the date over ln $(K_{max} - K_{min})$ v ln da/dN.

Fracture in Steels

Tests on 15 specimens of spheroidized eutectoid composition streel were carried out to evaluate the role of cyclic loading at net section stresses less than yield on subsequent tensile behaviour. Up to 200 cyclces in the range 0.1 to 0.9 of the yield stress had no detectable influence on the tensile behaviour. Detailed metallographic observations failed to reveal any evidence of carbide particle cracking or decohesion as a result of the cyclic loading.

Principal Investigator: C. J. Beevers (Engineering)

Supported by the Materials Research Laboratory/NSF.

Summaries of Other Related Work

Dynamic Properties of Structural Materials - J. Duffy (Engineering) - See Section 1.

X-Ray Topographic Techniques and Applications - B. Roessler (Engineering) - See Section 1.

SECTION 3

INTRODUCTION

Inorganic Glasses

The experimental research and theoretical investigations of inorganic glasses, performed during this period within the Inorganic Glasses Group, are reported.

A central focus in this research area is on structure and bonding in inorganic glasses. These studies include the first observation of an O^{17} NMR spectrum of an inorganic glass, B_2O_3, by which the existence of several distinct oxygen environments was shown. P. Bray has also obtained Si^{29} and B^{11} NMR spectra, shown them to be sensitive to structural groupings in silicate, borate and borosilicate glasses, and developed a structural model for them. Structural models for mixed alkali and mixed network glasses have been developed by W. Risen on the basis of vibrational spectral studies. J. Tauc has developed an energy-level model to explain contributions of features observed by photoemission to the fundamental optical absorption edge. Tauc has also concluded from his optical studies that the electronic states which determine the absorption edge in liquid sulfur are insensitive to higher order structural correlations. W. Risen investigated the molecular structural changes accompanying the glass transition in alkali metaphosphate glasses by Raman spectroscopy. P. Hess and M. Rutherford studied the structural changes required for liquid-liquid invisability and glass formation in alumino silicates.

Theoretical studies include the work of J. Gibbs on the structure and formation of network glasses by consideration of the sol-gel transition. The Nagel-Tauc theory of metallic glass formation has been extended, and the ordering of ions in the liquid, which enhances the glass-forming ability of an alloy, has been shown by J. Tauc to follow from this theory and to be due to differences in the pseudopotentials of the metal and metalloid. A theoretical approach to understanding the mixed alkali effect on ion transport properties was developed by W. Risen. R. Cole has developed methods for interpreting and understanding interactions in ionically conducting materials by time domain spectroscopy. The work of J. Gibbs on spin glass transitions, and on the behavior of relaxation time in linear polymeric glasses near the glass transition and its relationship to the configurational entropy is reported.

SECTION 3

Inorganic Glasses

Individual Contributions

Silicate Liquid Immiscibility in Aluminous Melts

Small amounts of alumina depress the critical temperatures of immiscible silicate melts and thereby render metastable the two liquid field. Inorder to investigate this effect in detail, immiscible melts were produced in some SiO_2-rich compositions in the SiO_2-TiO_2-CaO-MgO system. The T-x coordinates of these two liquids were determined for compositions containing 0,3,6,7,8,9 wt.% Al_2O_3. The critical temperatures for these compositions are greater than 1700 degrees C for 0% Al_2O_3 and approximately 1550-1600°C for 6% Al_2O_3. The two liquid field disappears at 9% Al_2O_3. The two coexisting liquids include a SiO_2-rich liquid containing minor amounts of CaO,MgO and TiO_2 and a relatively SiO_2-poor liquid containing high concentrations of CaO,MgO and TiO_2. Al_2O_3 is fractionated into the SiO_2-poor melt. This is in contrast with the behavior of Al_2O_3 in alkali-bearing immiscible silicate melts wherein the Al_2O_3 is fractionated into the high SiO melt. The mole ratio of $K_2O + Na_2O/Al_2O_3$ in the SiO_2 -rich melts is close to unity, indicating that the aluminum occurs in oxygen coordinated tetrahedral sites within the melt. In the alkali-free melts cited above aluminum fractionates into the SiO_2-poor melt because it apparently occurs as an octahedral coordinated cation and cannot enter the tectosilicate-like structured SiO_2-rich liquid. If this is true, then presence of calcium alone is not sufficient to induce aluminum to enter tetrahedrally coordinated oxygen sites.

Principal Investigator: P. C. Hess (Geological Sciences)

Personnel: M. Wood (Geological Sciences) and F. Ryerson (Geological Sciences)

Publications: Hess,, P.C.,"Structure of Silicate Melts," Canadian Mineralogist, in press.

Hess, P.C., "Equations of State for Ideal Silicate Melts," (Abs). GAC, p. 57, Edmonton, Alberta.

Rutherford, M.J., Hess, P.C., Ryerson, F.J., Campbell, H.W.,

and Dick, P.A., "Chemistry, Origin and Petrogenetic Implications of Lunar Granite and Monzonite," Proc. Lunar Sci., Conf. 7th, in press.

Supported by the Materials Research Laboratory/NSF.

Immiscibility in Complex Silicate Glasses

Silicate liquid immiscibility studies on both simple and complex chemical systems are gradually providing insight into the structural and thermodynamic properties of silicate glasses. The work on simple metal oxide silica systems is reported on elsewhere in the issue by Hess. Work on the more complex chemical systems provides additional information on the structure of the glasses in that the partitioning of the elements between the glasses is a function of the structure. It also provides some very basic geological information in so far as silicate liquid immiscibility occurs in natural glasses.

Silicate liquid immiscibility has been demonstrated in the K_2O-Al_2O_3-FeO-SiO_2 system, but does not occur in one atmosphere experiments on the Na_2O analogue of this system. Experiments on an ocean ridge basalt composition with a high Na_2O/K_2O ratio have just been completed however, and immiscibility does occur in glasses remaining after approximately 85 percent crystallization. The Na_2O/K_2O ratio in the acidic composition glass is about 2/1. The alkali composition of the starting glass is being changed systematically in experiments now underway to determine the behavior and affect of the alkalis more precisely.

The ability of the various metal oxides such as Na_2O,CaO,MgO, TiO_2,FeO and P_2O_5, to enhance or inhibit the onset of immiscibility in silcate glasses is variable as indicated by their behavior in simple MO-SiO_2 systems. This is being investigated further, but theory and preliminary experiments indicate that variations in the H_2O content of glasses has a much greater effect on the development of immiscibility. The equipment to investigate in detail the effects of both total pressure and P_{H_2O} (X_{H_2O}) has been built and is now being tested.

Principal Investigator: M. J. Rutherford (Geological Sciences)

Personnel: H. Campbell (Geological Sciences), P. Dick (Geological Sciences) and S. Dixon (Geological Sciences)

Publications: Rutherford, M. J., "The Chemistry, Origin and Petrogenetic Implications of Lunar Granites and Monzonite," Proc. Lunar Sci. Conf. 7th, 18 pages, 1976.

Rutherford, M. J. (with others), "Lunar Granites: a discussion: Lunar Science VII, pp. 364-366.

Supported by the Materials Research Laboratory/NSF and National Aeronautics and Space Administration.

Absorption Edge of Liquid Sulfur

The absorption coefficient of liquid sulfur was measured in the energy range from 1.2 to 2.6eV with the aim to detect the influence of structural correlation (rings or chains) on the electronic properties. It was found that the absorption coefficient is a continuous function of temperature in the temperature range studied (120 to 200°C). In particular, it has no discontinuity at the polymerization temperature (160°C) if the transmission data are corrected for the anomalous light scattering occurring at the onset of the polymerization temperature; this effect was reported previously by Zanini and Tauc. The conclusion of the study of the absorption edge in liquid sulfur is that the electronic states which determine the optical edge are insensitive to higher order structural correlations.

Principal Investigator: J. Tauc (Engineering)

Personnel: M. Zanini (Engineering)

Publications: Zanini, M., and Tauc, J., "Temperature Dependence of the Absorption Edge of Liquid Sulfur," J. Non-Crystalline Solids (in press).

Supported by the Materials Research Laboratory/NSF.

Electronic Structure and the Formation of Metallic Glasses

Nagel and Tauc's theory of metallic glass formation was further developed and tested. It was realized that the glass forming ability of an alloy is enhanced by the ordering of ions in the liquid. In particular, in the M-X (metal-metalloid) alloys there is some experimental

evidence that close to the glass transition temperature there are no X-X nearest neighbors. Nagel and Tauc showed that such correlation effects follow from their theory because of the differences in the pseudopotentials of the metal and the metalloid.

Photoemission measurements were started on a new group of glasses based on binary alloys of two transition metals (M-M glasses) such as Nb:Ni or Cu:Zr. The aim of this work is to provide experimental data for an understanding of the role of the d-bands in the glass formation. In these alloys, the Fermi level is inside or close to the d-bands, as distinguished from the metal-metalloid glasses in which the d-bands are often relatively deep below the Fermi level.

Principal Investigator: J. Tauc (Engineering)

Personnel: S. R. Nagel (Engineering)

Publications: Tauc, J., and Nagel, S. R., "Electronic Structure and Stability of Metallic Glasses," Comments on Solid State Physics, 7, 25 (1976).

Nagel, R. R. and Tauc, J., "Stability of Metallic Glasses: Photoemission Studies and a New Electronic Model for Glass Stability," Proceedings of the Second International Conference on Rapidly Quenched Metals," Cambridge, MA 1975 (in press).

Nagel, S. R. and Tauc, J., "Influence of Electronic Structure on Glass Formating Ability of Alloys," Third International Conference on Liquid Metals, Bristol, 1976 (to be published).

Nagel, S. R. and Tauc, J., "Correlations in Binary Liquid and Glassy Metals (to be published).

Nagel, S. R., Tauc, J., and Giessen, B. C., "Photoemission Study of Nb:Ni glasses (in preparation).

Supported by the National Science Foundation, the United States Army (ARO), and the Materials Research Laboratory/NSF.

Electronic Structure of Oxide Glasses

A comparison is made between the X-ray photoemission spectra of the core levels and the valence band of a high purity soda-lime-silica glass (21.3wt.%Na_2O--5.2wt.%CaO--73.5wt.%SiO_2) with those for fused silica. In the valence band of fused silica three peaks are observed whereas in the compound glass an additional peak is found above the high

binding energy edge of the valence band. The presence of non-bridging oxygen in the soda-lime silica glass not only broadens the oxygen core level asymmetrically to lower binding energy, but also broadens the lowest energy peak in the valence band. It is this latter broadening which certainly contributes to the shift in the fundamental optical absorption edge to lower energy in this glass with respect to pure SiO_2. An energy-level model is proposed for this glass.[2] The diffusion of Na^+ ions to the surface is also observed.

Principal Investigator: J. Tauc (Engineering and Physics)

Personnel: S. R. Nagel (Engineering)

Publications: Nagel, S. R., Tauc, J., and Bagley, B. G., "X-ray Photoemission Study of Soda-Lime-Silica Glass," Solid State Communications, 20, 245 (1976).

Supported by the National Science Foundation and the Materials Research Laboratory/NSF.

B^{11} NMR in the Glass System K_2O-B_2O_3-P_2O_5

The boron-oxygen coordination glasses of the system K_2O-B_2O_3-P_2O_5 has been studied. The primary purpose of this work was to compare the values of the fraction N_4 of four-coordinated boron atoms measured by NMR and by Raman Spectroscopy. Initial B^{11} NMR studies of glasses having the compositions of those investigated by the Raman technique have yielded values of N_4 that disagree radically in some cases with the published values. A complete analysis of N_4 data will be made to understand the structural groupings in this system, including (BPO_4) units.

B^{11} NMR in the Glass System Na_2O-B_2O_3-SiO_2

Despite the technological importance of glasses in the system Na_2O-B_2O_3-SiO_2, no clear model or quantitative understanding has previously been developed for the structure and chemical bonding in these materials. However, the boron-oxygen coordination has now been determined from the B^{11} NMR spectra for the glasses. By choosing the sample compositions more systematically, it is now possible to provide a quantitative understanding of boron-oxygen coordination as a function of compositions. About fifty samples were made spanning the glass-forming region with the compositions arranged so that the glasses were grouped into five families, each family having the same K value but different R values, where K = molar% SiO_2/molar% B_2O_3, and R = molar% Na_2O/

molar% B_2O_3. The fraction N_4 of boron atoms in four-coordination and the fraction N_{3A} of boron atoms in coordination with one or two non-bridging oxygens were measured. The values of N_4 when plotted as a function of R for fixed K indicate that $N_4 = R$ for $R < R_{max}$, N_4 reaches a maximum at $R = R_{max}$, and decreases linearly as R increases for $R > R_{max}$. The values of N_{4max} and R_{max} for each family appear to increase slightly with K. $N_{3A} = 0$ for all the families when $R < R_{max}$, and N_{3A} increases for fixed K in the region $R > R_{max}$. To interpret these results, a structural model has been proposed. This structural model permits the determination of the values of N_4, N_{3A}, and N_{4max} of a certain K family from a knowledge of the glass composition (i.e. from K and R).

O^{17} NMR in Borate Glasses

The first observation of O^{17} NMR in glass has been reported for pure B_2O_3 glass enriched to 37 percent O^{17}. An analysis of the quadrupolar-broadened spectrum indicates the presence of two distinct oxygen environment: i) an oxygen site characterized by a very small distribution in its Hamiltonian parameters; and ii) an oxygen site with a large distribution in the value of the asymmetry parameter (η). These results are consistent with the boroxol ring model of J. Krogh-Moe.

This work is now being extended to the compounds and glasses of the system Li_2O-B_2O_3. This system was chosen because of its large region of glass formation and relative ease of preparation of both the compounds and the corresponding glasses. The objective of this work is to be able to distinguish between the various oxygen environments present in these materials. In particular, the next material chosen for study is the compound $Li_2O.B_2O_3$. It is known from X-ray diffraction that lithium metaborate consists of a chain-type structure of boron and oxygen containing an equal number of bridging and non-bridging oxygens. It is expected that the O^{17} NMR will be able to distinguish between these two environments.

Si^{29} NMR in K_2O-SiO_2 Glasses

Silicon-29 NMR spectroscopy has been used to identify the silicon-oxygen groupings in a series of potassium silicate glasses. Since Si^{29} has a spin of ½, it has no electrical quadrupole moment or interaction. Hence, the chemical shift interaction was used in this investigation. The potassium silicate system was initially chosen for this study because the dipolar broadening of the Si^{29} resonance should be much less in these glasses than in the corresponding sodium and lithium silicate glasses; small shifts and structure in the resonance lines should be better resolved. It had been reported that silicate glasses have the least disorder in their structure of all the alkali silicate glasses.

It was found that the NMR lineshapes for the glasses generally revealed asymmetric chemical shifts, and that the lineshapes changed with composition and agreed with the lineshapes in the compounds at compositions which form crystalline compounds. Distinct and chracteristic chemical shift anisotropies were observed in the spectra for the meta-, di-, and tetrasilicate compositions. The anisotropies apparently arise from the differing numbers of non-bridging oxygens in the SiO_4 tetrahedra. For cristobalite, in which there are no non-bridging oxygens, a symmetric Si^{29} NMR line was observed.

The Si^{29} chemical shifts and linewidths are small, and work is in progress to perform experiments using a superconducting magnet capable of producing magnetic fields up to 80,000G. This would facilitate the determination of the chemical shift parameters which characterize the various silicon-oxygen tetrahedral configurations.

Si^{29} NMR has proved to be a useful tool for studying the silicon environement in the potassium silicate glass system. Work to complete the K_2O-SiO_2 system, and extension to other systems - in particular the sodium and lithium silicate systems - is forthcoming.

Principal Investigator: P. J. Bray (Physics)

Personnel: Y. H. Yun (Physics), S. A. Feller (Physics), I. A. Harris, Jr., (Physics) and F. Bucholtz (Physics).

Publications: Jellison, Jr., G. E., Feller, S. A., and Bray, P. J., "NMR Powder Patterns for Integer-Spin Nuclei in the Presence of Asymmetric Quadrupole Effects," Submitted to J. Mag. Res.

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Yun, Y. H., and Bray, P. J., "Nuclear Magnetic Resonance Studies of Boron Coordination in Na_2O-B_2O_3-SiO_2 Glasses," Abstract submitted to the American Ceramic Society 79th Meeting, Chicago (1977).

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Jellison, Jr., G. E., Panek, L. W., Bray, P. J., and Rouse, Gr., G. E., "Determination of Structure and Bonding in Vitreous B_2O_3 by Means of B10, B11, and 017 NMR," accepted for publication in J. Chem. Phys.

Panek, L. W., and Bray, P. J., "NMR of Tl^{205} in Tl_2O-SiO_2, Tl_2O-GeO_2, and Tl_2O-B_2O_3 Glasses," accepted for publication in the Journal of Chemical Physics.

Bray, P. J., and Hendrickson, J. R., "Dependence of the Mixed-Alkali Effect on Ion Masses," J. Non-Cryst. Solids, 21, 297 (1976).

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Park, M. S., Kim, K. S., and Bray, P. J., "B^{11}NMR Studies of the System MgO-B_2O_3," submitted to Phys. Chem. Glasses.

Panek, L. W., Exarhos, G. J., Bray, P. J., and Risen, W. M., "NMR and Infrared Study of Cation Motion in Vitreous and Polycrystalline $TlPO_3$," submitted to J. Non-Cryst. Solids.

Supported by the National Science Foundation and the Materials Research Laboratory/NSF.

The Mixed Alkali Effect: A Theoretical Approach

The compositional dependence of transport properties of ionic oxide glass series of the type $x(Ma_2O)(1-x)(Mb_2O)$. (A_pO_q) is a central aspect of the mixed alkali effect, in which one cation is replaced systematically by the other cation. An approach to understanding this dependence has been developed, based on the relationship of the probability of occurrence of the relevant cooperative processes to the compositional dependence of the effective activation free energies for these processes. The compositional dependences of the activation free energies are calculated using the physical model of the regular solution for the two component glass system. This treatment leads to satisfactory agreement with available experimental data, including "pre-exponential' terms as well as activation enthalpy or energy terms. Combination of a specific molecular model, which employs the far

infrared observed cation vibrational (ion motion) frequencies for calculating activation energies for ionic diffusion and ionic conductivitity, with this general treatment not only leads to agreement but also provides a method for employing spectroscopic and local bonding information in understanding the compositional dependence of other mixed alkali glass properties. This approach has been applied to ionic conductivity in the $(M_2O:M'_2O).6.7\ SiO_2$ systems where M:M' are Cs:Na, Rb:Cs, Cs:K, and Na:Cs, and Li:Cs, and to the K:Na, K:Li, and Li:Na systems of the $(M_2O:M'_2O).2SiO_2$ composition to date, Additional applications to mixed modifier glass sytems have been initiated.

Principal Investigator: W. M. Risen, Jr. (Chemistry)

Personnel: G. B. Rouse, (Chemistry) and J. M. Gordon (Chemistry)

Publications: Proceedings of the IV International Conference of the Physics of Non-Crystalline Solids, Intertech Publications, 1976.

Supported by the United States Navy and the Materials Research Laboratory/NSF.

Ionic Oxide Glass Spectral Studies

Spectroscopic studies of ionic oxide glasses and their crystalline analogs have been carried out on three systems of materials. The first is the mixed network modifier (mixed alkali) metaphosphate and metaarenate glass systems. The previously reported observations of the metaphosphate systems, leading to the conclusions of microscopic homogeneity, cation-site interaction constancy through the series, and averaging of the influence of the changing cation effect on the network modes, have been subject of analysis. The analysis proceeded on the basis of the local mode (or decoupled network mode, DCN) approach and indicate that although the mass, charge and size factors manifest themselves, the effect on network bond-angles is the dominant effect. The analogous experiments on metaarsenate glasses have been initiated, based on the recently completed study of the complete spectra of the amorphous and crystalline forms of the pure metaarsenate materials.

The ion-motion spectra of metaarsenate glasses $(MAsO_3)(g\ell)$, have been related to the glass transitions, measured in this period by differential calorimetry, and to changes in Raman intensity of inchain and pendant network modes. The Raman

studies of these glasses show relative proportions of linear chain and ring structures in the metaarsenates by analogy to the crystalline forms, and the changes in these proportions are shown to give rise to the relative intensity changes of the Raman bands as a function of temperature.

Principal Investigator: W. M. Risen, Jr. (Chemistry)

Personnel: G. B. Rouse (Chemistry) and A. Paeglis (Chemistry)

Publications: Paeglis, A. and Risen, Jr., W. M., "Vibrational Spectra and Glass Transitions in Alkali Metaarsentate Glasses," J. Phys. Chem. (in submission).

Supported by the National Science Foundation and the United States Navy.

Statistical Mecahnics of Supercooled Liquids and Glasses

The structure of network glasses has been investigated theoretically by consideration of the nature of the sol-gel transition by which some of them may be formed in the laboratory and by which all may be formed in a thought-experiment. The classical calculation by Stockmayer of the most probable distribution of polymer molecular weights in the sol fraction both above and below the critical extent of reaction has been shown to require considerable modifaction if one wishes to extract information on the gel phase as well. This modification has been carried out, and a result different from that of Stockmayer obtained for the high molecaular weight tail of the distribution. Additionally, the mean distribution has been calculated exactly and found to be different from the most probable distribution in the high molecular weight tail. This difference has been interpreted in terms the finite size of the system.

The Edwards-Anderson model for random systems has been studied. Its Hamiltonian is $H = \Sigma - J_{ij}\,\sigma_i\sigma_j$ where $J_{ij} = J_o + uJ_1$ and u is a Gaussian parameter. The free energy and specific heat have been calculated for the case $J_o = 0$, also known as spin glass. In three dimensions no transition appears. In two dimensions, indications of a cusp were found. Work on the case $J + 0$ is in progress.

The behavior of the relaxation time, τ, in plymers near the glass transition is being studied by the linear response method. This should render more rigorous the result obtained heuristically by Adams and Gibbs, $\tau \propto \exp(C/ST)$, where S is the configurational entropy which approaches zero as we approach the glass temperature.

Principal Investigator: J. H. Gibbs (Chemistry)

Personnel: E. S. Donoghue (Chemistry), R. V. Ditzian (Chemistry) and A. M. Dunker (Chemistry)

Publications: Gordon, J. M., Gibbs, J. H., and Fleming, P. D., "The Hard Sphere 'glass transition'," J. Chem. Phys. Vol. 65(1976) 2271.

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Supported by the Materials Research Laboratory/NSF.

Time Domain Spectroscopy of Dielectric Materials

Work was begun on refinements and extensions of previously developed methods, together with applications to study of a variety of dielectric materials. Useful procedures have been developed for determination of frequency dependent permeability of magnetically isotropic instances and permittivity of materials with appreciable ohmic conductance. Some preliminary measurements on Zeolites have demonstrated the feasibility of studying the state of adsorbed water in these powders and work will be continued in collaboration with K. M. Foster, now at the Laboratory for Biomedical Engineering at the University of Pennsylvania.

Other experiments directed at study of interactions between ions and dipoles in conducting systems have been started, the motivation being to test the Onsager and Hubbard theory

of the kinetic depolarization effect. In this as yet unpublished work, the permittivity of the system is predicted to decrease linearly with ionic conductance and in proportion to the dipole relaxation time T. In work of S. E. Lovell in this laboratory in 1957, such an effect of conductance was found in H_2SO_4 solutions, but the theoretical predictions could not be tested because the relaxation process occurred at too high frequencies to be studied properly. Our TDS methods make this possible, and preliminary results have demonstrated a dipole relaxation of Debye form with T = 340 ps which together with the earlier data gives results in semi-quantitative agreement with the Onsager-Hubbard theory.

Principal Investigator: R. H. Cole (Chemistry)

Personnel: D. G. Hall (Chemistry)

Publication: "Time-Domain Spectroscopy of Dielectric Materials," IEEE Trans. Instrum. and Measu. IM-25, 371 (1976)

(Text of invited paper given at Conference on Precision Electrical Measurements, Boulder, Col., June 28, 1976).

Supported by the Materials Research Laboratory/NSF.

SECTION 4

INTRODUCTION

Chemisorption on Metallic Surfaces

During the period 1975-76 the Surface Group had engaged in a series of studies concerning the electronic, magnetic, structural and chemical properties of solid surfaces. As described below, the work has ranged from experimental studies of chemisorption to theoretical investigations of the basic physical characteristics of the substrate. Metallic surfaces have continued to be of central interest to the Group but the methods are not limited to these systems and preliminary work on other materials has been initiated.

The experimental results reported by Stiles and Estrup concern chemisorption on single-crystal transition metal surfaces which are examined under ultra-high vacuum conditions, by a variety of spectroscopic techniques. The data are used to construct detailed, microscopic models of the interaction of molecules and atoms in the overlayer. Risen has studied the coordination of ligands to metal ions and atoms in ionomers and in metal clusters; the bonding appears to be analogous to that occurring in chemisorption. In a theoretical study Quinn has examined the response of a metal surface to a varying electric field and the dependence of the response on the electron density profile. One consequence of the work is an improved understanding of the optical reflectivity of a surface with and without a chemisorbed layer. Ying has used the spin density funtional formalism to study the magnetic properties of a metallic surface. The behavior is found to be quite different from the bulk and may be important in adsorption and desorption phenomena.

SECTION 4

Chemisorption on Metallic Surfaces

Individual Contributions

Optical Spectroscopy of Surfaces

We have continued to improve the instrumentation of universal ultra-high vacuum for the study of surfaces, by optical techniques. Results for gases on W surfaces have been obtained with improved signal to noise. The data have been interpreted within the framework of the McIntyre-Aspnes model of an absorbed layer on the surface. This has been done with data taken with both p and s polarization. The raw data show strong similarities for the two cases; the p polarization results appear only as scaled down versions of the s polarization and near identical energies are obtained for both polarizations. Feibelmann has pointed out however, that as the p polarization has a component of the electric field perpendicular to the surface, the assumptions of the McIntyre-Aspnes model of a local field should be invalid, and that one might expect drastically different behavior. This has not been observed to date, and we are continuing to study these phenomena.

Principal Investigator: P. J. Stiles

Personnel: M. A. Passler (Physics) and G. Blanchet (Physics)

Publications: None

Supported by the Materials Research Laboratory/NSF.

Dynamic Response of a Metal Surface

The current density induced in a finite solid by a spatially varying electric field is given by $j(z) = \int dz' \sigma(z,z') E(z')$. In contrast to the situation in an infinite translationally invariant medium, $\sigma(z,z')$ depends on z and z' individually, not just on their difference. We have evaluated $\sigma(z,z")$ using a hydrodynamic model for a jellium surface with an arbitrary electron density profile. The surface plasma excitations, including the higher multipole

excitations, can be obtained from $\sigma(z,z')$ by studying self-sustaining oscillations. The optical reflectivity and change in reflectivity caused by chemisorption are currently being investigated.

Principal Investigators: J. J. Quinn (Physics) and S. C. Ying (Physics).

Personnel: A. Equiluz (Physics), S. Das Sarma (Physics)

Publications: Equiluz, A. and Quinn J. J., "Hydrodynamic Model for Surface Plasmons in Metals and Degenerate Semiconductors," Phys. Rev. B14, 1347 (1976).

Equiluz, A. and Quinn, J. J., "Magnetoplasma Surface Waves in Solids with Diffuse Electron Density Profiles," Phys. Rev. B13, 4299 (1976).

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Ting, C. S., Ying, S. C. and Quinn, J. J., "Plasmon Assisted Free Carrier Absorption," Proc. Int. Conf. on Semiconductor, Rome, to appear.

Supported by the National Science Foundation.

Experimental Studies of Chemisorption

The application of high resolution Auger electron spectroscopy (AES) to the study of bonding in chemisorbed layers has been investigated. By correlating the AES spectra with ESCA (UPS and XPS) data, also obtained in this laboratory, efforts are underway to characterize the specific electronic transitions responsible for the spectral features and to elucidate the final-state ("relaxation") effects. The results show that an AES spectrum may permit the identification of multiple binding states and a distinction between molecular and dissociative adsorption. For example, it has been found that carbon monoxide dissociates on transition metals of groups V and VI (e.g. Ta, Mo, W) but not on those of group VIII (e.g. Ir, Ni, Pt).

Studies of the chemisorption of CO, CO_2 and O_2 on Mo(100) have been extended to include the behavior at low temperature. These investigations have used LEED, AES, work function and flash desoprtion measurements. In addition, electron stimulated desorption (ESD) has - for the first time - been successfully incorporated without any modification of the LEED optics, so that a direct correlation with the standard techniques has become possible. Among the conclusions of the study are (i) CO and CO_2 dissociate completely at room termperature but not at low temperature ($\sim -100^{o}C$). (ii) The lateral interactions between C and O atoms are strong but must be indirect and involve the metal substrate. (iii) Molecular overlayers of CO and CO_2 hinder O_2 adsorption, while, at room temperature, preadsorbed C and O do not prevent subsequent oxygen adsorption.

Principal Investigator: P. J. Estrup (Physics & Chemistry)

Personnel: T. E. Felter (Physics), S. Semancik (Physics) and G. Robertshaw (Physics)

Publications: Felter, T. E. and Estrup P. J., "The Chemisorption of CO, CO_2 and O_2 on Mo(100)," Am. Phys. Soc. Bull. 21, No. 7, 939 (1976).

Felter, T. E. and Estrup, P. J., "Improved Method for LEED Intensity Measurements," Rev. Sci. Instrum. 47, 158 (1976).

Felter, T. E. and Estrup, P. J., "Model of β-CO: Dissociative Adsorption," Surface Sci. 54, 179 (1976).

Estrup, P. J., "Two-Dimensional Structure of Adsorbed Layers," Am. Phys. Soc. Bull. 21, 218 (1976).

Supported by the Materials Research Laboratory/NSF.

Theoretical Study of Metallic Surfaces

We have applied the spin density functional formalism to study the magnetic behavior of metallic surfaces. It is found that the combined effect of the change of exchange coupling and the density of state function of the surfaces region can lead to a surface magnetic behavior quite different from that in the bulk. In particular, a surface transition to a ferromagnetic state can precede the bulk transition. This has been demonstrated explicitly for the jellium model of a metal-vacuum interface. Formal equations have been developed for the study of transition

metal surfaces. Near the transition temperature, there exists large spin fluctuations which can play an important role in the adsorption and desorption of atoms on metallic surfaces. A set of hydrodynamic equations has been derived for the study in these spin fluctuations.

Principal Investigator: S. C. Ying (Physics)

Personnel: None

Publications: Kahn, L., Beál-Monod, M. T., and Ying, S. C., "Spin Density Functional Formalism for Surface Susceptibility of a Nearly Ferromagnetic Metal," Solid State Communication, 18, 359, (1976).

Supported by the Materials Research Laboratory/NSF, the National Science Foundation and the United States Navy.

Formation and Study of Metal-Ligand Chemisorption Models in Ionomers

We have shown that the isolation of transition metal ions in PFSA (perfluorocarbonsulfonic acid) ionomers places them in a support environment in which they can be subjected to heating and evacuation to remove initially coordinated ligands. The resultant supported but coordinatively unsaturated ions become individual reactive sites such that the introduction of a gaseous molecule can lead to formation of a species of the type M-L, which can, in turn, model a chemisportion species. We have formed isolated Rh(III)-NO, Rh(III)-CO, Ru(III)-NO, Ru(III)-CO, and Ru(III), Rh(III), Co(II) and Fe(II)-C_2H_4 species, and have studied them by infrared spectroscopy to identify the vibrational properties of the molecules so attached.

In addition, formation of very small clusters of metal ions, metal salts, and metal atoms have been formed in these PFSA ionomers and found to be reactive with CO, NO, H_2 and C_2H_4 to form both weakly and strongly bound species. ESCA as well as infrared and laser Raman spectroscopy are employed to identify the reactive species and reaction products.

Principal Investigator: William M. Risen, Jr. (Chemistry)

Personnel: S. Peluso (Chemistry) and A. Tsatsas (Chemistry)

Supported by the Materials Research Laboratory/NSF and the Office of Naval Research.

SECTION 5

Chalcogenide Materials

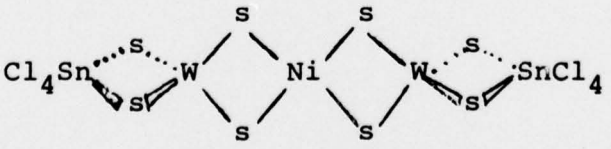
Inorganic Monomers and Polymers: Synthesis and Properties

The preparation of square planar complexes of the type $[M(M'S_4)_2]^{2-}$, where M = a d^8 metal ion and M' = Mo or W, has been extended to M = Au(III). Higher-yield synthetic techniques have been achieved for the M = Ni(II), Pd(II) and Pt(II) compounds reported last year.

Improved cyclic voltammograms have shown that the Mo and W complexes of Ni(II) and Pd(II) undergo electrochemically reversible one-electron reductions. Chemical reduction may be effected with excess $NaBH_4$. The reduced species are air-sensitive and have not been successfully isolated. No esr spectrum was observed at room temperature from $[Ni(MoS_4)_2]^{3-}$; low-temperature work is in progress.

Irreversible oxidation of the dianions are observed electrochemically, but $[Pt(WS_4)_2]^{2-}$ reacts with Br_2 to afford a new species formulated as $[Pt(WS_4)_2Br_2]^{2-}$. This compound will be used to study the existence of partially oxidized chain compounds analogous to the platinum cyanides.

Chemical reactivity of the terminal sulfur atoms in the $[M(M'S_4)_2]^{2-}$ complexes has been shown by reaction of $[Ni(WS_4)_2]^{2-}$ with α, α'-dibromo-o-xylene and with $SnCl_4$. The latter complex thus has a linear chain of five metal atoms bridged by sulfurs:



Principal Investigator: K. Callahan (Chemistry)

Personnel: P.A. Piliero (Chemistry), A.B. Fischer (Chemistry) and J. Grossman (Chemistry)

Publications: Piliero, P.A., and Callahan, K.P., "Tetrathiometalate Complexes of d^8 Metal Ions: Synthesis, Chemistry and Electrochemistry," in preparation for submission to Inorganic Chemistry.

Supported by the Materials Research Laboratory/NSF and the Research Corporation.

Investigations of Solar Cells Based on Chalcocite (Cu_2S) and $CuInS_2$.

Photovoltaic solar cells having solar energy conversion efficiencies in excess of 4% have been fabricated by depositing a thin (~900 angstroms) layer of chalcocite (Cu_2S) on n-type silicon. The open circuit voltage is in excess of 0.4V on some of the cells which implies that a hetero-junction has been formed between n-silicon (E_G~1.1eV) and the p-Cu_2S(E_G~1.2eV). It is, however, difficult to prove that the Cu_2S is contributing to the short circuit current as it should if it is a true heterojunction because the bandgaps are nearly equal and it is almost impossible to distinguish features in the spectral response curve which can be attributed to the chalcocite. Attempts are continuing to increase the efficiency mainly by adding an antireflection coating and improving the contact to the chalcocite.

We have also continued our study of p-Cu_2S/nCdS cells with attention focused on post-fabrication treatments which are necessary to optimize the cell characteristics. We have observed that luminescence intensity decreases in the course of "copper treatment" and increases in the course of simple heat treatment in air. Copper treatment consists of deposition of a thin (~50 angstrom) layer of Cu on the Cu_2S and heating the system in air.

It has been postulated by other investigators that the Cu diffuses into the Cu_2S and drives composition toward being copper-rich. The fact that luminescence intensity decreases after copper treatment suggest that this explanation is not valid because copper should reduce the Cu-vacancy concentration and it is known that luminescence decreases as Cu-vacancy concentration increases.

As part of our study of p-Cu_2S/nCdS cells, we have begun to grow CdS single crystals epitaxially on germanium substrates. Such crystals are reputedly the highest quality large area crystals ever grown, and solar cells fabricated on these crystals at the Philips Laboratories in Holland have the highest reported efficiencies for cells of this type. Our purpose is to increase the efficiency of such cells beyond the 8% reported by Philips.

Single crystals of $CuInS_2$ have been grown by iodine vapor transport in a closed tube. Auger spectroscopy indicates that they are of high quality.

Principal Investigator: J. J. Loferski (Engineering)

Personnel: J. Shewchun, Visiting Professor (Engineering), R. Arnott (Engineering), E. A. DeMeo (Engineering), E. E. Crisman (Engineering), R. Beaulieu (Engineering), H. L. Hwang (Engineering), C. C. Wu (Engineering), M. Arienzo (Engineering).

Publications: Mittleman, S. D., Loferski, J. J., Shewchun, J., and DeMeo, E. A., "Cathodoluminescence in the Cu-S System," Bull. of the American Phys. Soc., Series II, Vol. 21, 591 (1976).

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Loferski, J. J., "Material Properties and Polycrystalline Solar Cell Characteristics," Proc. Workshop on Low Cost Polycrystalline Solar Cells, Dallas, Texas, May 1976.

Loferski, J. J., Shewchun, J., DeMeo, E. A., Arnott, R., Crisman, E. E., Beaulieu, R., Hwang, H. L., and Wu, C. C., "Characteristics of Chalcocite (Cu_xS) Films Produced by Different Methods and Some Properties of Solar Cells Made from Such Films," Proc. First International Workshop on Solar Electricity, Toulouse, France, March 1976.

Supported by the National Science Foundation/Rann Solar Energy Conversion Program and the United States Energy Research Development Administration.

Frenkel Defects in Mixed Zinc Subgroup Chalcogenide Semiconductor Single Crystals

Photoluminescence spectra in CdS irradiated at 10 K and 80 K with 250 keV to 1.0 MeV monoenergetic electrons were studied in the wavelength region 4800 - 5500A. Irradiation results in a decrease of intensity of all observed lines as well as changes in the intensities of individual line relative to each other. These changes are interpreted in terms of the

radiative and non-radiative recombination centres introduced by the irradiation. The course of annealing in the range 100 - 300 K of the spectra was studied for various bombarding electron energies. In all cases annealing to room temperature results in a substantial recovery of some of the observed lines. However, the course of annealing varies markedly with electron energy. As this energy increases the magnitude of 120 - 160 K annealing stage increases relative to the 100 - 120 K and 170 - 220 K annealing stages. These changes can be correlated with increases in the ratio of Cd to S displacements. On this basis, the 120 - 160 K annealing stage is assigned to migration of Cd interstitials. "Superannealing" of the edge emission band was observed. It was found that UV light and 80 keV electrons beam do not affect the course of low-temperature annealing.

Principal Investigator: J. J. Loferski (Engineering)

Personnel: H. Rzewuski, Z. Werner and A. Kozanecki, (Institute of Nuclear Research, Warsaw, Poland).

Publications: Rzewuski, H., Werner, Z., Kozanecki, A., and Loferski, J. J., "Photoluminescence in CdS Irradiated with High Energy Electrons," International Conference on Radiation Defects in Semiconductors, Dubrovnik, Yugoslavia, September 1976.

Supported by the National Science Foundation Foreign Currency Program through Maria Sklodowska-Curie (Poland-U.S.) Fund.

Mixed Anion Compounds of the Transition Metals

Oxyfluorides

Single crystals of $NH_4V_3O_6F$ have been synthesized by allowing ammonium vanadate, vanadium metal, and ammonium hydrogen fluoride to react under a hydrostatic pressure of 1.33 kbars at 450°C. The product crystallizes in the monoclinic system, space group P2/c, with a_o=8.251(4)Å, b_o = 4.939(1)Å, c_o = 6.986 (1)Å, and β = 100.5(3)°, ρ_{calcd}=3.39 g cm^{-3}, ρ_{exptl}= 3.36(2) g cm^{-3} for Z=2. The structure consists of octahedra linked together by corner, edge, and face sharing to form 6A thick sheets that extend parallel to (100). Between these sheets there are zigzag chains of ammonium ions. The compound exhibits Curie-Weiss behavior between 240 and 450K, with a P_{eff} of 1.83 BM, and has a room-temperature resistivity of 10^8 Ω-cm, indicating the localized character of the electrons.

Indium Thiosphosphides

Crystals of $In_{2/3}PS_3$ were grown by chemical vapor transport of the elements from a charge zone maintained at 630°C and and a growth zone at 560°C. The crystals were characterized by chemical x-ray, and densitometric techniques. $In_{2/3}PS_3$ is structurally related to the $M^{II}PS_3$ thiosphosphides. The compound is an insulator and has an optical absorption edge of 3.1(1) e.V.

Platinum Sulfoselenides

Both powder and single crystal samples of several phases of composition $PtSe_{2-x}S_x$ $2 \leq x \leq 0$ were prepared by either sealed tube techniques or chemical vapor transport using phosphorus as the transport agent. The phases were characterized by x-ray and densitometric techniques. The electrical behavior between 77° and 300°K is reported.

Copper Iron Thiogermanides

Single crystals of the solid solution series $CuFe_xGe_{1-x}S_2$ ($0.5<x<1.0$) have been prepared by the chemical vapor transport technique. X-ray diffraction analysis and density measurements have indicated that all members of this system crystallize with the chalcopyrite structure. Mössbauer spectra show that these crystals contain both iron (II) and iron (III) on tetrahedral sites and that the iron concentration agrees with that determined by chemical analysis. Magnetic susceptibilities for x=0.53 display antiferromagnetic behavior. The Néel temperature of 12°K and an effective moment of 5.0 BM is observed, which approaches the calculated spin-only moment of 4.92 BM. As x increases, deviations from spin-only behavior occur, indicating complex magnetic interactions.

Chalcogenides

Platinum Ditelluride

Single crystals of $PdTe_2$ have been grown from the melt at a temperature of 800°C by means of a modified Bridgeman technique. Characterization studies of the crystals included density determinations and x-ray analysis. The crystals were found to be metallic, and the sign of the carriers from Seebeck measurements was ascertained to be positive.

Paladium Rhodium Ditelluride

The system $Pd_{1-x}Rh_xTe_2$ ($0 \leq 0.4$) was found to crystallize at ambient pressure with the cadmium iodide structure. Reactions carried out with a high pressure belt apparatus at 1000°C and 60 kbars pressure resulted in a complete transformation

to the pyrite structure for $x \geq 0.6$.

Principal Investigator: A. Wold (Chemistry and Engineering)

Personnel: F. Pintchovski (Chemistry), S. Soled (Chemistry), E. McCarron (Chemistry), R. Korenstein (Chemistry), J. Ackermann (Chemistry), A. Lyons (Chemistry), and D. Schleich (Chemistry)

Bernard Tanguy, Chargé de Recherche (CNRS), Josik Portier, Maître de Recherche (CNRS), Michel Pezal, Chargé de Recherche (CNRS), R. Brec, Chargé de Recherche (CNRS), A. Tressaud, Maître de Recherche, (CNRS), L. Lozano, Assistant (CNRS), P. Hagenmuller Professor, (Bordeaux), E. Kostiner, Associate Professor, University of Connecticut.

Publications: Pintchovski, F., Soled, S., and Wold, A., "Preparation, Crystal Structure, and Properties of $NH_4V_3O_6F$," Inorg. Chem., 15, 330 (1976).

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Lyons, A., Scheich, D., and Wold, A., "Crystal Growth and Characterization of $PdTe_2$," Mat. Res. Bull., 11, 1155 (1976).

McCarron, E., Korenstein, R., and Wold, A., "High Pressure Phase Transformation Studies of the System $Pd_{1-x}Rh_xTe_2$," Mat. Res. Bull., 11, 1457 (1976)

Supported by the Materials Research Laboratory/NSF, and the National Science Foundation/Centré National d'la Research Scientifiqué, and the United States Army, Triangle Park, North Carolina.

Transport and Optical Properties of Semiconductors

Germanium Photoconductivity

More detailed measurements of the photoconductivity in germanium have been combined with an extension of the theory of Appel to include carrier anisotropy and valence band degeneracy. Measurements over the range 21 to 298 K were continued; analysis still showed that the observed decrease in mobility with increasing electron-hole density (up to the range 10^{17} to 10^{18} cm^{-3}) was greater than predicted by theory.

At lower temperatures (1.6-10 K) infrared measurements of the absorption by photo-induced electrons and holes in the range 3.1-4.2 m were undertaken in order to test the cross section which had been assumed in normalizing the earlier measurements. These measurements showed that the cross section measured by others for doped material is much larger than the cross section when electrons and holes in high density are present only (doping level in the 10^{12} cm^{-3} range); the cross section at 3.39 m for electrons and holes of density in the range 10^{17} cm^{-3}, is 4.5×10^{-17} cm^2 instead of the value assumed earlier of 1.5×10^{-16} cm^{-2}.

Energy Band Behavior in Non-isoelectronic Solid Solutions of Semiconductors

In cooperation with J. E. Fischer of University of Pennsylvania and J. A. Van Vechten of IBM, Yorktown Heights, we have considered the extension of the quantum dielectric theory to non-isoelectronic semiconductor solid solutions, such as PbS-Cds, $CuInSe_2$-ZnSe and GaP-ZnS, comparing the results with the measurements made at several laboratories, including at Brown for the last systems mentioned. Agreement is good for the systems noted and for several other systems of the same type, when the theoretical and experimental values of the amount of bowing in the plot of energy gap with composition are compared.

Energy Gap and Transport Properties of Quaternary Compounds

Studies of the carrier mobility as a function of temperature, and detailed studies of the optical absorption in the vicinity of the band gap and below were initiated for quaternary compounds of the type $I_2IIIV\,VI_4$, with Cu_2ZnGeS_4 being a particular example. Single crystals of these materials were prepared in the MRL Materials Preparation Facility under the direction of Professor A. Wold. In early measurements, it was determined that the mobilities were of the order of 1 cm^2/V-sec and doping densities were in the 10^{19} cm^{-3} range, for that material.

Principal Investigator: M. Glicksman (Engineering)

Personnel: S. Mittleman (Engineering), J. Meyer (Physics) I. Mykyta (Physics), K. Burbank (Engineering), and P. Joshi (Physics).

Publications: Glicksman, M., Gurnee, M. N., Meyer, J. R., "Transport Properties of High Density Electron-Hole Plasmas at Low Temperatures," Lecture Notes in Physics 57, Physics of Highly Excited States in Solids (ed. M. Ueta and Y. Nishina), pp. 219-229 (Springer Verlag, Berlin, 1976).

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Supported by the Materials Research Laboratory/NSF, and the National Science Foundation.

SECTION 6

Alloy Design and Synthesis of Microstructures for Specific Properties

Boundary and Particle Strengthening in Steels

The evaluation of previously reported experimental results was carried to the strain hardening-range. The strain-hardening behavior of spheroidized steels was examined in terms of continuum and quasi-continuum models based on the requirement that continuity be maintained at various boundaries in the two-phase polycrystals. For plastic strains up to 3.5% the flow stress is given by:

$$\sigma_{e_r} = \sigma_{e_{p=0}} + \Delta\sigma_g + \Delta\sigma^s + \Delta\sigma^i$$

where the increase in flow stress appears to be composed of contributions arising from (i) dislocations stored in the materials for (a) stastical $\Delta\sigma^s$ and (b) geometrical reasons $\Delta\sigma_g$ and (ii) an average back stress, $\Delta\sigma^i$, predominantly due to the presence of the unrelaxed plastic strain discontinuity between the ferrite matrix and the cementite particles. The latter contribution, which is a large fraction of the total strain-hardening increment, increases rapidly with strain up to a plastic strain of 3.5% and remains approximately constant thereafter. The attainment of the maximum value of the back stress corresponds to the observed transition in the overall strain-hardening rate ("double-n" behavior). The experimentally determined components of the hardening increment due to the geometrically necessary dislocations agree well with the predictions of Ashby's theory.

At strains greater than 3.5%, the average back stress remains approximately constant and the geometrically necessary dislocation density increases only slighty with strain. This indicates a deviation from Ashby's theory which predicts a continuous increase of this dislocation population with strain. The strain-hardening increments at these strain levels therefore appear to be controlled mainly by the increase in the statistical dislocation population.

Principal Investigator: J. Gurland (Engineering)

Personnel: Dr. L. Anand, Research Laboratory, United States Steel Corporation, Monoreville, Pennsylvania.

Publications: Anand, L. and Gurland, J., "Effect of Internal Boundaries on the Yield Strength of Spheroidized Steels," Met. Trans., (1976), 7A, pp. 191-197.

Anand, L. and Gurland, J., "Strain Hardening of Spheroidized High Carbon Steels," Acta. Met. (1976) pp. 901-909.

Supported by the United States Energy Research and Development Administration.

Reaction Bonding of Silicon Nitride

Continued efforts at relating a thorough microstructural study of reaction bonded Si_3N_4 to both processing conditions and mechanical properties has allowed the "design" of Si_3N_4 for optimum room temperature transverse rupture strength and high temperature creep resistance.

The chemistry and microstructural aspects of the "new" material were studied and the details of bonding and the mechanisms of formation of the various microconstituents were determined.

Work has centered on utilizing "design: to synthesize the best material and on measuring its properties. This has led to very promising results.

Principal Investigator: M. H. Richman (Engineering)

Personnel: J.O. Edwards (Chemistry), S. C. Danforth (Engineering), J. W. Fogarty (Engineering) Dr. Hamlin Jennings, Department of Materials, University of Cape Town.

Publications: Danforth, S.C., Jennings, H.M., and Richman, M. H., "The Ladder Microconstituent of Silicon Nitride," Metallography, 9 (1976) 361.

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Supported by the Materials Research Laboratory/ARPA.

Thermally Activated Flow of Commercially Pure Titanium During Anodic Dissolution

The flow stress of commercially pure (100A) titanium polycrystals has been studied while undergoing anodic dissolution in a methanol - 10% HNO_3 polishing solution Flat tensile specimens of 0.050 inch sheet were used in low strain-rate creep tests and stress relaxation tests. Decreases in flow stress on the order of 5% have been found. The magnitude of the drop is directly related to the removal rate and is found to be low relative to that for self-diffusion. A divacancy method is assumed to be operative with divacancies introduced as the specimen is dissolved. Activation volume measurements have also been made.

Principal Investigator: D. H. Avery

Personnel: E. Savage (Engineering)

Publications: Avery, D. H., and Savage, E., "Thermally Activated Flow of Commercially Pure Titanium During Anodic Dissolution," Proceedings Third Int. Conf. on Stength of Materials.

Savage, E., "An Investigation of the Role of the Surface in the Mechanical Behavior of Polycrystalline Titanium," Masters Thesis, Brown University 1976.

Supported by the Materials Research Laboratory/ARPA.

The Effect of Chemical Composition on the Thermo-Mechanical Strengthening of β Titanium

The effect of β stabilizing elements Cr-V-Mo in the ratio 10:7:3.5 on the thermo-mechanical strengthening of β Titanium has been investigated. Six heats were prepared of Ti:3% Al and total β stabilizers ranging from 15.5 to 20.5 in 1% increments. Specimens were cold swaged 18, 48, 84, and 95%. After 95% Coldwork, tensile strength

increased from 1.5 GN/m^2 (p 218 ksi) to 1.72 GN/m^2 (251 ksi) with increasing β stabilizers. After aging the β lean ally showed the highest strength, 2.50 GN/m^2 (362 ksi) compared to 2.24 GN/m^2 (325 ksi) for the β rich alloy.

Principal Investigator: D. H. Avery (Engineering)

Personnel: F. Tatar (Engineering)

Publications: Avery, D. H., and Polan, N., "Mechanical Thermal Processing of a β Titanium Alloy," Trans AIME V 7A 1976 p. 323.

Avery, D. H., Polan, N., and Tatar, F., "Effect of Chemical Composition on the Thermomenchanical Strengthening of β titanium," Proc. Third Int. Conf. on the Mechanical Behavior of Materials.

Supported by the Materials Research Laboratory/ARPA and the Council of Scientific International Research.

Mechanisms of Particle Strengthening

The present experimental program is a continuation of the work of J. Gurland and L. Anand on particle strengthening in spheroidized steels and that of R. Asaro concerned with dispersion hardened Ni-Cr alloys. Specific attention was paid to the contribution to the overall strain-hardening caused by the non-deforming carbides or oxides. A quasi-continuum model, which takes into account the plastic strain discontinuities at the various two phase boundaries, was used to interpret experimental measurements of strain hardening, cyclic deformation response, and the Bauschinger effect. The measurements and the model suggest that a significant part of the hardening can be represented by a quantity $\Delta\sigma^i$ that acts sensibly like a long range internal stess. $\Delta\sigma^i$ is proposed in the model to be an increasing function of strain which saturates at some particular strain value as 3.5% for spherodized steels or 2% for Ni-20 Cr dispersion hardened with 3 vol. percent Y_2O_3. The experiments suggest that the saturation value for $\Delta\sigma^i$ is in fact particle size (as well as volume fraction) dependent - $\Delta\sigma^i$ increases with decreasing particle size for particle diameters in the range 0.2 - 1.0 μm. Furthermore, $\Delta\sigma^i$ increases less than linearly with plastic strain up to saturation with a rate that also increases with decreasing particle size. For the steels it was found that the saturation of $\Delta\sigma^i$ was indeed coincident with the so-called "double-n" behavior as suggested by Gurland and Anand. This observed behavior is being interpreted in terms of dislocation models for plastic relaxation at the particle-matrix interface. Furthermore, we are attempting

to use these measurements and our models to estimate the local stresses produced at or near the particle interfaces that influence both particle fracture and decohesion. In the course of this work, a very general formalism for evaluating Baushinger effects for various microstructures has also been developed.

Principal Investigator: R. J. Asaro (Engineering)

Personnel: Y. W. Chang (Engineering)

Publications: Asaro, R. J., "Reversible Plasticity and Work Hardening," appearing in "Advances in the Understanding of Work Hardening," ed. R. M. Pelloux and A. W. Thomson, ASM 1977.

Chang, Y. W., MS Thesis, in preparation, January 197[illegible]

Supported by the United States Energy Research and Development Administration and the National Science Foundation.

Summaries of Other Related Work

Microscale Fracture Mechanisms - J. Gurland (Engineering) - See Section 2.

Hardness and Fracture Strength of Cemented Carbides - J. Gurland (Engineering) - See Section 2.

SECTION 7

Plasmas in Solids

Optical Properties of Nonequilibrium Semiconductor Plasmas

The optical properties of dense nonequilibrium electron-hole plasmas in semiconductors have been experimentally studied in selected materials (InSb, $Hg_{1-x}Cd_xTe$, Ge). Such plasmas are generated from absorption of intense infrared laser radiation of subnanosecond duration and the optical properties of the transient plasma are examined during the excitation and the return to equilibrium of a system under study.

In the narrow-gap semiconductors, such as InSb and $Hg_{1-x}Cd_xTe$, the small electron effective masses near the conduction band edge cause the electron gas to become degenerate at relatively low carrier densities ($n \sim 10^{17}$ cm^{-3}). One directly observable consequence resulting from a laser induced "bandfilling" effect is the dynamic shift of the optical absorption edge to higher photon energies. We have used modelocked high-pressure CO and CO_2 lasers with photon energies near the absorption edge of InSb and $Hg_{.80}Cd_{.20}Te$ to induce large enhanced transparencies for laser pulses whose duration is short in comparison with the interband lifetimes. Under such conditons we have measured self-enhanced transparencies exceeding three orders of magnitude for subnanosecond laser pulses of intensities exceeding approximately 1 kW/cm^2. By using a weaker probe beam the interband recombination rates have been studied.

Our investigations have also included the study of the contribution to the dielectric constant by free carriers from laser induced changes of the surface reflectivity in a semiconductor. In these experiments intense laser pulses of picosecond duration have been used to generate a dense electron-hole plasma in Ge. When the instantaneous plasma frequency exceeds the frequency of a weak infrared probe laser beam very nearly total reflection of the probe beam occurs. We have used this phenomena to study the features of the free carrier plasma edge and diffusion dynamics at high carrier densities in Ge. The unique advantage of such studies, presently extended to other semiconductors, is the possibility of examining the dynamics of dense semiconductor plasmas without interference from impurity effects.

Principal Investigator: A. V. Nurmikko (Engineering)

Personnel: A. V. Nurmikko

Publications: A. V. Nurmikko, "Saturation of Optical Absorption in InSb," Opt. Comm. 16, 365 (1976).

Nurmikko, A. V., "Nonlinear Abosprtion at 10.6 μm in $Hg_{1-x}Cd_xTe$," Opt. Comm. 18, 522 (1976).

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Jamison, S. A., Nurmikko, A. V., and Gerritsen, H. J., "Transient Spectroscopy of Semiconductor Plasmas," 1976 Annual Meeting of the Optical Society of American, Tucson.

Supported by the Materials Research Laboratory/NSF.

Two-Dimensional Plasmas

Recent interest in two-dimensional plasmas has continued. Studies at low density seem to indicate that the universality of the minimum metallic conductivity in 2 dimensions has not been found to be true. The simple Anderson localization is not an adequate picture of the effect of potential fluctuations. Some other parameter, which may only involve some other moment of the distribution seems to play a role. These studies continue. Effective masses were measured on other surfaces and show no unusual behavior, except on the 811 surface. The degeneracies on the 111 and 110 surface were not as expected, which must be interpreted as a new ground state. The effect of surface scattering is under investigation to determine what parameters play a role in the scattering of electrons. This involves samples from many world sources. The 811 surface continues to be mysterious, with the presence of a very light carriers, lighter than what one would expect from the band structure of bulk Si.

Principal Investigator: P. J. Stiles (Physics)

Personnel: T. Theis (Physics), T. Cole (Physics) and A. A. Lakhani (Physics)

Publications: Lakhani, A. A. and Stiles, P. J., "Modification of the Magnetoconductance of a Two-Dimensional Electron Gas by Altering the Boundary Conditons in the Third Dimension," Solid State Comm, 16, 993 (1975).

Sjostrand, M. E. and Stiles, P. J., "The Channel Conductivity in n-Type Si Inversion Layers at Very Low Electron Densities," Solid State Comm. 16, 903 (1975).

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Sjostrand, M. E., Cole, T., and Stiles, P. J., "Low Temperature Saturation of the Channel Conductivity in Si Inversion Layers," Surf. Sci. 58, 72 (1976) and Proc. of Int. Conf. on Elec. Prop. of Quasi-Two-Dimensional Systens, ed. Quinn and Stiles (1976, North Holland).

Sjostrand, M. E., Cole, T., and Stiles, P. J., "Activated Channel Conductivity in Si Inversion Layers at High Temperatures," Surf. Sci. 58, 91 (1976) and Proc. of Int. Conf. on Elec. Prop. of Quasi-Two Dimensional Systems, ed. Quinn and Stiles (1976, North Holland).

Lakhani, A. A. and Stiles, P. J., "Effect of Substrate Bias on the Mobility and Scattering Time of Electrons in Si Inversion Layers," Surf. Sci. 58, 193 (1976) and Proc. of Int. Conf. on Elec. Prop. of Quasi-Two-Dimensional Systems, ed.

Supported by the Materials Research Laboratory/NSF/ARPA, the National Science Foundation and the United States Navy.

Plasmas in Solids

The memory function method was applied to study the transport properties of metallic plasmas and in particular the quasi-two dimesnional electron gas in the inversion layer of semiconductor surfaces. We have clarified the role played by the impurities in the influence of many-body effects on transport properties such as cyclotron resonances.

Principal Investigator: S. C. Ying (Physics)

Personnel: F. Crowne (Physics)

Publications: Ting, C. S., Quinn, J. J., Ying, S. C., "Infrared Cyclotron Resonance in Semiconductivity Surface Inversional Layers," Phys. Rev. Letter, 37, 215 (1976).

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SECTION 8

Low Temperature Properties of Materials

Fermi Surface of Strontium Titanate

Measurements have been made of magneto-thermal oscillations of niobiun-doped strontium titanate at low temperatures and high magnetic fields in an effort to determine the Fermi surface of this material. Interest in this experiment results from the fact that superconductivity in this semiconductor has been explained in the past by the presumed existence of a large electron-electron interaction produced by inter-valley scattering among several electron pockets near the edges of the Brillouin zone. More recent band calculations by Mattheiss, however, predict that the conduction band mimimum is located at the zone center. Because of the cubic to tetragonal phase transition at 105°K the present measurements are not able to provide an unambiguous determination of the shape of the band minimum. Nonetheless, the model of several equivalent ellipsoids near the zone boundary is incompatible with the data and supports the prediction of a conduction band at the zone center.

Principal Investigator: G. Seidel (Physics)

Personnel: B. Gregory (Physics) and J. Arthur (Physics)

Publications: None

Supported by the National Science Foundation.

Thermodynamic Properties of He^3-He^4 Mixtures

Using a superconducting microwave cavity to measure the density of liquid He^3-He^4 mixtures in the temperature range 0.1°K to 0.5°K, we are able to investigate several important properties of the He^3 quasiparticles. The thermal expansion of the mixture is dependent on the nature of the He^3 quasiparticle dispersion relation

$$\varepsilon(k) = \varepsilon_o + \frac{h^2k^2}{2m} + \gamma(hk)^4$$

Both the parameters m and γ and their pressure derivatives enter the expansion coefficient. By accurately determining the terms in the density that are dependent linearly and quadratically on temperature at the saturated vapor pressure we have been able to make estimates of these parameters and find them in reasonable agreement with theoretical predictions. Work is in progress to refine the measurements and extend them to other pressures.

Principal Investigator: G. Seidel (Physics)

Personnel: L. Nagurney (Physics)

Publications: None

Supported by the National Science Foundation.

Studies of the Transmission of Phonons across Interfaces

Our previous work in this area was an experimental investigation of the transmission of phonons from classical solids (e.g., silicon) into quantum systems (i.e., liquid and solid helium, or solid hydrogen or deuterium). The results showed that in all cases the phonon transmission was much larger than expected from an acoustic theory. We have begun a theoretical study aimed at explaining this effect. Specifically, we have made calculations of the wave functions of helium atoms bound to a surface by a van der Waals force and have calculated the rate at which energy is absorbed by the atoms when the surface vibrates. These calculations show some promise of providing an explanation of the large phonon transmission, and are being continued.

Principal Investigator: H. J. Maris (Physics and Metals Research Laboratory)

Supported by the National Science Foundation and the Materials Research Laboratory.

Roton Second Sound

We have considered the general theory of second sound propagation, both when collision between elementary excitations do and when they do not conserve total number. Simple expressions are derived for the velocity in each case. Assuming that number conservation does hole for roton-roton collisons, the velocity of roton second sound was found to be $3kT/p_o$, where p_o is the momentum at the roton minimum. This compares with the earlier calculations of Khalatnikov and Chernikova

who obtained a velocity of $\sqrt{3}\ kT/p_o$. The Khalatnikov-Chernikova theory appears to contain an implicit assumption that there are sufficient number non-conserving collisions to maintain a zero chemical potential as the second sound propagates. This work is being extended to include an accurate experimental measurement of the velocity of roton second sound.

Principal Investigator: H. J. Maris (Physics and Metals Research Laboratory)

Personnel: R. Cline (Physics)

Publications: Maris, H. J., "Roton Second Sound," Phys. Rev. Lett. 36, 907 (1976).

Supported by the National Science Foundation and the Materials Research Laboratory.

Heat Pulses, Phonon Transport and Ultrasonic Wave Propagation in Solids

We have studied the effects on ballistically propagating phonons (heat pulses) of dislocations vibrating under the effect of ultrasonic waves propagating in the solid concurrently with the heat pulses. A detailed study was conducted on lithium fluoride. The most pronounced effect of this interaction is observed as a significant decrease of the amplitude of fast transverse phonons propagating in the < 110 > direction of an alkali halide. The experimental data are being analyzed in terms of microscopic mechanisms involving the difference in scattering of phonons by static and by vibrating dislocations.

Principal Investigator: C. Elbaum (Physics and Applied Mathematics)

Personnel: A. Hikata (Applied Mathematics)

Publications: None

Supported by the Materials Research Laboratory/NSF.

Phonon-Phonon Interactions in Liquid Helium-Four

Earlier studies of the propagation of ultrasonic waves in liquid helium-four, conducted at saturated vapor pressure, were extended to higher pressures (up to 20 Atm). These

studies were conducted for the purpose of relating measured phonon-phonon scattering with the phonon dispersion relation. Experimentally, the main emphasis in this study is on determining the dependence of changes ΔC, in sound velocity C, on frequency, in the temperature range $50mK \lesssim T \lesssim 400mK$. The experimental results were interpreted in terms of a model for phonon-phonon interactions using a dispersion relation of the form $\varepsilon = Cp(1 + \gamma p^2 + \ldots)$. The coefficient γ was determined earlier to be positive at saturated vapor pressure, with a value of 18×10^{37} c.g.s. units. In the present study γ was found to decrease with increasing pressure and to extrapolate to zero at a pressure of approximately 20 Atm.

Principal Investigator: C. Elbaum (Physics and Applied Mathematics)

Personnel: W. R. Junker (Physics)

Publications: Junker, W. R., and Elbaum, C., "Dependence of Sound Velocity in Liquid Helium-4 on Temperature, Pressure and Frequency; A Test of the Phonon Dispersion Relation," Phys. Lett. 57A, 432 (1976).

Supported by the Materials Research Laboratory/NSF.

Fluctuations in Type II Superconductors

Close to the upper critical field of a type II superconductor fluctuations in the number of electron pairs are one dimensional in nature. We examined theoretically the effect of such fluctuations on the transport properties of a clean type II superconductor in a magnetic field near its upper critical field and at a temperature $T > T_{CB}$.

We find, for example, that the fluctuation contribution to the longitudinal sound attenuation has the form

$$\alpha_{f\ell/\alpha_N} \underset{\sim}{\alpha} (\ell/\xi_0)\eta^{\frac{1}{2}}$$

where ℓ is the mean free path, ξ_0 is the coherence length and $\eta = (T - T_c(B)/T_c(B)$; this leads to a decrease in the attenuation, effectively smearing out the transition. Note the increase in the effect of fluctuations as the sample becomes purer.

We have also calculated the thermal conductivity and surface impedence: similar results are found.

Transport in Superfluid ^{3}He

The transport properties of superfluid ^{3}HeA have been studied in a generalised paramagnon model which we call the "Spin Fluctuation Dominance Model". Briefly, our attitude is that the scattering of the ^{3}He quasi particles is dominated by spin fluctuations exchange, the contribution of density fluctuations to the scattering is one order of magnitude smaller. As naive paramagnon theory is well known to over estimate the effect of forward scattering the partial wave scattering amplitudes associated with spin fluctuation exchange are left as free parameters which can be identified with the empirical amplitudes of the normal state.

We have used the model to calculate the viscosity, thermal diffusivity, spin relaxation time and spin diffusion tensor of ^{3}HeB, and the orbital viscosity, viscosity and thermal diffusivity of ^{3}HeA.

Principal Investigator: A. Houghton (Physics)

Personnel: M. C. Yalabik (Physics) and D. Allender (MRL)

Publications: Allender, A., and Houghton, A., "Quasi-One-Dimensional Fluctuation Contribution to Ultrasonic Attenuation in Clean Type II Superconductors above $T_c(B)$," Phys. Rev. B13, 3215 (1976).

Kadanoff, L. P., Yalabik, M. C., and Houghton, A., "Variational Approximations for Renormalisation Group Transformations," J. Stat. Phys. 14, 171 (1976).

Maki, K., and Houghton, A., "Relaxation and Transport Properties of Superfluid H -B (Spin Fluctuation Dominance Model," Phys. Rev., to be published.

Kadanoff, L. P., Yalabik, M. C., and Houghton, A., "Variational Approximations for Renormalization Group Transformations, Proc. Hungarian Acad. Sci. 97 (1976).

Maki, K., and Houghton, A., "Comment on Orbital Relaxation in ^{3}HeA," Proc. International Symposium on Superfluid ^{3}He, Sussex, England (1976), to be published.

Maki, K., and Houghton, A., "Relaxation and Transport in ^{3}HeB at Low Temperature (Spin Fluctuation Dominance Model," submitted to Phys. Letters.

Allender, D., Thompson, R. S., and Houghton, A., "One-Dimensional Fluctuation Contribution to Transport in Clean Type II Superconductors," submitted to Phys. Rev.

Cerdeira, H. A., Maki, K., and Houghton, A., "Transport Properties of Superfluid ^{3}He-A," submitted to Phys. Rev.

Supported by the Materials Research Laboratory/NSF.

SECTION 9

Pseudo One-Dimensional Conductors

Pseudo One-Dimensional Conductors

Experimental interst in quasi one-dimensional systems has been stimulated by experiments on the organic crystal, TTF-TCNQ, the polymer $(SN)_x$ the platinum salts $K_2[Pt(CN)_4]\ Br_{0.30} \cdot 3H_2O$ and by the Brown CdS result. We have been investigating the Luther-Peschel[1] and Luther-Emery[2] (LE) solutions of the Luttinger,[3] Mattis-Lieb[4] model of one-dimensional interacting fermions. The (LE) solution is obtained for one value of the large momentum parallel spin scattering coupling constant $U_{//}/2\pi\ v_F = -3/5$. It would be of great interest to generalize their result to other values of this coupling constant.

For $U_{//} = -2\pi\ v_F$, the spin density part of the (LE) Hamiltonian can be divided into two commuting parts. Using the boson representation of fermion operators,[1,6] H' can be diagonalized resulting in a pure gap. T' can be diagonalized at least formally by using a variation of the Mattis-Lieb[4] canonical transformation or by mapping T' into the Thirring model.[7] The point $U_{//} = -2\pi\ v_F$ is just at the lower bound of the physical region so that this exact solution may have no physical interpretation. However, with the solution at $U_{//}/2\pi\ v_F = -3/5$ it can be used to help determine properties of the solutions in the physical range.

To obtain solutions for the range of coupling constants connecting the two soluble points, we have defined operators for a renormalized fictitious fermion field on a rescaled length. Using these operators we can find the exact solutin for generalized $U_{//}$ of a problem with more degrees of freedom than the original model. We have a situation therefore in which we can find the exact solution of a problem with more degrees of freedom than the one we are trying to solve so that to retrieve the original problem we must remove some of the extra degrees of freedom. We expect that these additional degrees of freedom can be removed, perhaps by renormalization group methods or by methods such as those used

by H. U. Everts and H. Schulz, (8), or K. D. Shotte, (9) and that the energy spectrum and correlation functions of the (LE) model can be calculated for all values of $U_{//}$ in the physical region.

REFERENCES

(1) A. Luther and I. Peschel, Phys. Rev. B 9, 2911 (1974).
(2) A. Luther and V. J. Emregy, Phys. Rev. Letters 33, 589 (1974).
(3) J. M. Luttinger, J. Math. Phys. 4, 1154 (1963).
(4) D. C. Mattis and E. H. Lieb, J. Math. Phys. (N. Y.) 6, 304, (1965).
(5) L. N. Cooper and E. Berkcan, in preparation.
(6) D. C. Mattis, J. Math. Phys. (N. Y.) 15, 609 (1974).
(7) W. Thirring, Ann. of Phys. 3, 91 (1958).
(8) H. U. Everts and H. Schulz, A. Physik B 22, 285-294 (1975).
(9) K. D. Schotte, Z. Physik 230, 99-107 (1970).

Principal Investigator: L. N. Cooper (Physics).

Personnel: E. Berkcan (Physics).

Publications: Cooper, L. N., "Fermion Systems in Different Dimensions," Proceedings of the 1975 Lectures of International School for Subnuclear Physics (A. Zichichi, editor).

Cooper, L. N., "A New Solution for the One-Dimensional Electron Gas with Backward Scattering," (with E. Berkcan) in preparation.

Supported by the Materials Research Laboratory/ARPA/NSF.

Preparation and Properties Of Thin Films of Polydiacetylenes

Thin films of the diacetylene TCDU, whose composition is RC_4R with $R = -(CH_2)_4\ OCONHC_6H_5$ have been prepared by evaportion and subsequently polymerized by low intensity UV irradiation. Investigations by optical and electron microscopy, laser Raman and optical absorption spectroscopies on the monomer and polymer films indicate that amorphous forms of each have been prepared in the 25-600 Å thick range. This was confirmed by electron diffraction studies on the films. The spectral features of the films are dependent on the morphology of the sample, which changes with irradiation exposure and thermal treatment, and characteristic features are associated with the morphological states observed. A comparative study of the polymerization of TCDU monomer crystals shows certain features in common with the films. Raman spectra of 25 Å thick films of the TCDU polymer were obtained.

Principal Investigator: W. M. Risen, Jr. (Chemistry)

Personnel: S. K. Bahl (Chemistry) and C. Tzinis (Chemistry)

Publications: Bahl, S. K., Baughman, R. H., and Risen, Jr., W. M., "Properties of Thin Films of Polydiacetylenes," J. Polym. Sci. (Poly Phys.) in submission.

Supported by the National Science Foundation and the United States Navy (ONR).

Nonohmic Conductivity Behavior of Polydiacetylenes

The electrical properties of the solid state polymerized diacetylene, R-C≡C-C≡C-R, where R is C_6H_5-NH-CO-O-CH_2-, have been examined on large single crystal fibers. The conductivity was determined at 300°K as resistance as a function of field and shows ohmic behavior at fields lower than 10^3 V/cm. The dc conductivity of these materials is low ($\sim 10^{-10} \Omega^{-1}cm^{-1}$), and they behave as intrinsic semiconductors with a band gap of ca 2 eV. Nonohmic behavior is observed at higher fields up to 1.5×10^3 V/cm. The functional dependences observed are consistent with a mechanism involving trap-modified space-charge limited current with the traps distributed uniformly in energy. The resonance Raman spectrum of these fibers is field-dependent and shows shifts of bands associated with vibrations of the polymer backbone along which electron-delocalization occurs. The field dependence of the Raman spectra have been related to the space charge effcts in the polymers.

Principal Investigators: W. M. Risen, Jr. (Chemistry)

Personnel: S. K. Bahl (Chemistry) and C. Tzinis (Chemistry)

Supported by the Materials Research Laboratory/NSF and the United States Navy (ONR).

Pseudo-One-Dimensional Systems

i) We have studied the electrical properties of polysulfur nitride $(SN)_x$ near its superconducting transition, with special emphasis on the fluctuations in conductivity above the transition temperature, T_c. An analysis of the temperature dependence of the excess conductivity has revealed that $(SN)_x$ is "one-dimensional" with respect to the superconducting coherence length, but does not

consist of independent, "atomic diameter" chains. The dominant "wire diameter" determined from these measurements is several hundred angstroms. (ii) We have studied the anisotropies of the optical properties and of electronic transport in plastically deformed cadmium sulfide to probe the electronic properties of this material. In particular, investigations were made of optical transmission and reflectivity in the region of the fundamental energy gap, using polarized light. These measurements were carried out as a function of several variables, namely: The angle between the light polarization direction and various crystal directions relevant to the plastic deformation; (ii) The amount of plastic strain; (iii) Temperature. Electrical conductivity was measured as a function of crystal direction and of temperature. On the basis of the experimental results a model was suggested to explain the observed features in terms of dislocation energy bands.

Principal Investigator: C. Elbaum (Physics and Applied Mathematics)

Personnel: R. Civiak (Materials Research Laboratory), W. Junker (Physics), C. Gough (Physics, Visiting Faculty from the University of Birmingham, England), and P. Merchant (Physics)

Publications: Civiak, R. L., Elbaum, C., Junker, W., Gough, C., Kao, H. I., Nichols, L. F., and Labes, M. M., "Fluctuation-Induced Conductivity above the Superconducting Transition Temperature in Polysulfur Nitide, $(SN)_x$," Solid State Comm. 18, 1205 (1976).

Merchant, P. and Elbaum, C., "Optical and Electronic Transport Anisotropies in Plastically Deformed CdS," Solid State Comm. 20, 775 (1976).

Supported by the National Science Foundation and the Advanced Research Projects Agency.

SECTION 10

Other Research

The Dynamic Response of Highly Stretched Polymers

Work has continued on the behavior of stretched rubber. The two problems being investigated are the anomalous response of rubber at stretch ratios in excess of about 3.5 where the effects of crystallinity result in an increase in the apparent modulus of the material as the axial stress relaxes, and the formation of tensile shock fronts and compressive shock tails in stretched rubber filaments.

The main advances that have been made during the year on the first problem have been partly theoretical in that a mathematical model of this type of behavior has been established and partly exerimental where it has been shown that as might be expected increasing the temperatures inhibits the appearance of crystallinity so that higher stretch ratios are required before the anomalous region is reached. Also that after stress relaxation has continued for some time, the crystallization process ceases and the material has a normal response to further relaxation of stress. A second experimental investigation has been carried out on the response of rubber specimens which have been stretched and then subjected to a step torque. The response here as in the case of the dynamic tests showed the effect of crystallization at stretch ratios in excess of 3.5.

Further experimental and theoretical work on shock waves in stretched rubber has been carried out and has been described in the Ph.D. thesis of Dr. S. Shih

Principal Investigators: H. Kolsky (Applied Mathematics) and A. C. Pipkin (Applied Mathematics)

Personnel: B. K. Min (Engineering), S. Shih (Engineering), and R. Stanton (Applied Mathematics)

Publications: None

Supported by the Materials Research Laboratory/ARPA.

Hydrogen Diffusion in Metals

Most available data for diffusion of hydrogen isotopes in fcc metals show Arrhenius behavior with pre-exponential factors which exhibit the classical inverse square-root mass dependence but with activation energies U which show the anomalous behavior $U_H > U_D > U_T$. It is shown that this behavior may be understood in terms of a quantum rate theory based on Gaussian wave packet ensembles in which the straight-line Arrhenius behavior arises from the opposing effects of quantum statistics and tunneling.

Polymers

A highly idealized model of a long chain molecule with internal energy barriers and under applied tension has been studied both analytically and by computer simulation. Equilibrium properties are computed exactly on the basis of equilibrium statistical mechanics. In the fully-extended and stretched state the model exhibits a transition of behavior, over a narrow range of temperature, from that appropriate to a harmonic crystal at low temperature levels to that characteristic of a polymer at higher temperature levels. The computer simulation procedure uses the Langevin equation and yields equilibrium values which agree well with the theoretical equation of state. The observer barrier crossing rates under equilibrium conditions agree reasonably well with a simple rate theory formulation although there are some systematic deviations. Computer simulation tests at constant cooling rate show "freezing" of the length at a non-equilibrium value at sufficiently high rates of cooling. Comparison is made with the theory of Volkenstein and Ptitsyn; there is qualitative agreement but substantial quantitative discrepancies.

Principal Investigator: J. H. Weiner (Engineering)

Personnel: M. Pear (Physics)

Publications: Weiner, J. H., "Anaomalous Isotope Effect for Hydrogen Diffusion," Phys. Rev. B., November 15, 1976.

Weiner, J. H., and Pear, M., "Computer Simulation of Conformational Transitions in an Idealized Polymer Model," Macromolecules, forthcoming.

Supported by the National Science Foundation and the American Gas Association.

Thermal Expansion Instability in Plastics

The thermal expansion of some polymers has been found to be a transient phenomenon. During the transition

following an increase in temperature the creep rate has been found to be much greater than after stabilization. Experiments were performed to find polymers which do not exhibit this behavior and to determine the cause.

The behavior has been found in polyurethane and epoxy resin, both high and low cross-linked. It was not observed in polyethylene. Experiments have shown the behavior to be due to small changes in moisture content. Results of creep studies suggest that the effect of temperature on creep rate is largely due to the state of expansion of the material--rather than temperature or moisture content.

Principal Investigator: W. N. Findley (Engineering)

Personnel: R. Mark (Engineering) and R. M. Reed (Engineering)

Publications: Manuscript by Mark and Findley prepared.

Supported by the National Science Foundation.

Cation Motion in Dry and Solvated Mono- and Divalent Cation Containing Zeolites X and Y

Far infrared spectra of dry synthetic zeolites X and Y have been shown to contain ion motion bands for Li^+, K^+, Rb^+, Cs^+, Ag^+, Ca^{+2}, Sr^{+2}, and Ba^{+2}, which have been assigned to the sodalite-cage sites in these materials. Site I and site II cation vibrational bands overlap and form the dominant features in monovalent cation-exchanged spectra, and a site III band has been observed in the CsY zeolite. The fact that cation-motion bands are at higher frequency on X than on Y zeolites has been related to the X- framework charge-distribution. Solvation of the zeolites with H_2O and polar organic solvents diminishes the ion-motion features and results in new spectral features, which vary with adsorbent dielectric constant, due to ion-motion in a solvation shell, whose structure also depends on the nature of the adsorbant. The implications of the cation vibrational frequencies for the mechanism of ionic conduction are considered in terms of a simple pseudo-free ion model. Ion transport in Y zeolites, which have a large number of vacant cation sites so that each jump may be considered an independent event, is adequately explained by this model, but ion transport in X zeolites is best interpreted in terms of cooperative effects.

Principal Investigator: W. M. Risen, Jr. (Chemistry)

Personnel: W. M. Butler (Chemistry)

Publications: Butler, W. M., MacAllister, W., Angell, C. L., and Risen, Jr., W. M., "Far Infrared Study of Cation Motion in Dry and Solvated Mono- and Di-valent Zeolites X and Y," J. Phys. Chem., in press (1976).

Supported by the Materials Research Laboratory/NSF and the United States Navy/ONR.

Ion Motion in Na-β-Alumina and its K^+, Ag^+, Tl^+, Sr^{+2}, Ca^{+2} and Several Transition Metal-Exchanged Derivatives

The far infrared spectra of powdered forms of x Na $0.11Al_2O_3$ ($x \simeq 1.2$-1.8) and of the K^+, Ag^+, Tl^+-exchanged analogs have been determined for materials from low to nearly complete cation exchange. The successive exchange method and a site-symmetry interpretation have permitted identification and assignment of the cation-β structure bands corresponding to vibrations at the Beevers-Ross (BR, a BR, and mO (mid-oxygen) sites. For Na-β-alumina and its K analog, BR and mO vibrations are formed, while for the Ag and Tl analogs, BR, a BR and mO bands are observed. The refletance spectra of the Na, K, Rb, and Cs forms, obtained from the (001) face of large crystals, and the low frequency polarized Raman spectra of crystals of Na, K. Ag and Tl forms have been analyzed. The cation-motion frequencies identified have been employed to analyze proposed mechanisms of ion-transport in these superionic conductors.

The effect on structure and ion-motion frequencies caused by the introduction of divalent ions has been investigated by vibrational spectroscopy, and, in the case of transition metal exchange, visible spectroscopy to determine the effective crystal field strength and its relation to ion-site vibrations.

Principal Investigator: W. M. Risen, Jr. (Chemistry)

Personnel: W. M. Butler (Chemistry)

Publications: Butler, W. M. and Risen, Jr., W. M., "The Far Infrared Spectra of Sodium-β-Alumina and its K^+, Rb^+, Cs^+ and Ag^+ and Tl^+ Analogs," in "Superionic Conductors," ed. G. D. Mahan and W. L. Roth, Plenum Press, New York, 1976, p. 372 ff.

Butler, W. M. and Risen, Jr., W. M., "Ion Motion in Sodium-β-Alumina and its Cation-exchanged Analogs," J. Sol. St. Chem. (1977) in submission.

Supported by the Materials Research Laboratory/NSF and the United States Navy/ONR.

Interaction of Mechanical and Electrical Imperfections in Solar Cells and the Fabrication of Improved Gallium Arsenide Solar Cells

An infrared transmission microscope has been activated for the study of structural defects in silicon and gallium arsenide wafers from which solar cells are to be fabricated. To date the system has been used principally to study silicon wafers.

The main emphasis of the program has been on the fabrication of gallium arsenide p/n juntion cells by the alloy process. A p-type GaAs wafer is covered with a thin (~2000 angstrom) layer of Sn and heated to about 600°C.for a few minutes. Some GaAs dissolves in the tin and when the system is cooled rapidly, a regrown layer of Sn saturated GaAs forms on the substrate. We have calculated that this regrown layer should have thicknesses in the range of several hundred anstroms if the Sn layer is originally 2000Å thick and if the wafer had been heated to 600°C. The thickenss of the regrown n-type layer can be controlled by controlling the thickness of the Sn and the alloying temperature. If the n-region thickness can be held to a few hundred angstroms, it should be possible to produce GaAs cells of solar energy efficiency comparable to that of $Al_xGa_{1-x}As$, GaAs cells because in both cases, the effect of losses of light generated carriers to the surface would be substantially reduced. To date we have produced p/n junction rectifiers by this method, but have not yet observed the anticipated photovoltaic effect.

Principal Investigators: J. J. Loferski (Engineering) and B. Roessler (Engineering)

Personnel: E. E. Crisman (Engineering), Y. Pierre (Engineering), Y. Ercil (Engineering), and W. Oates (Engineering)

Publications: Loferski, J. J., Roessler, B. Crisman, E., Pierre, Y., and Ercil, Y., "Methods of Improving the Efficiency of Photovoltaic Cells," Eleventh Semiannual Report-NASA, Grant No. NGR 40-002-093, June 1976.

Supported by the Materials Research Laboratory/NSF and the National Aeronautics and Space Administration.

Combined Stress Creep at Elevated Temperatures

Objective: The objective of this study is to determine the influence of temperature on the creep of polymers and to develop suitable theories for variable temperature.

Approach: Experiments were performed under combined tension and torsion at elevated temperatures on a polyurethane plastic and polyethylene in the nonlinear range under combinations of tension and torsion. Experiments under varying temperature have been performed to provide information on suitability of theory for variable temperature.

Many experiments have been made on several plastics in which rising and falling temperature histories have been imposed during creep. A method of prediction of creep under variable temperature has been evaluated.

Principal Investigator: W. N. Findley (Engineering)

Personnel: R. Mark (Engineering) and R. M. Reed (Engineering)

Publications: Findley, W. N., Lai, J. S. and Onaran, K., "Creep and Relaxation of Nonlinear Viscoelastic Materials," North-Holland Publishing Company, Amsterdam, 1976.

Supported by the National Science Foundation.

Subsequent Yield Surfaces for Steel

Objective: To study the nature of the yield surface and subsequent yield surfaces for steel, combinations of tension, torsion, compression are applied to tubular specimens to determine the yield point under various combined stresses both before and after yielding.

Progress:

(i) The effect of plastic strain on the yield surface has been investigated for 304L stainless steel in quadrants 1 and 4 of axial stress-shear space.

(ii) Initial and subsequent yield surfaces for SAE 1017 annealed mild steel have been found in all four quadrants of σ , τ space. Both load and strain control tests were conducted. Information on upper and lower yield points, constrained flow tests, normality, convexity, ageing, corners, cross effects and Bauschinger effects is available.

(iii) Initial and subsequent yield surface tests for SAE 1018 cold drawn steel have been completed. Analysis is in progress.

Principal Investigator: W. N. Findley (Engineering)

Personnel: R. M. Reed (Engineering) and M. J. Michno, Jr., (Union Carbide Corporation)

Publications: Michno, N. J., and Findley, W. N.,"An Historical Perspective of Yield Surface Investigations for Metals," International Journal of Nonlinear Mechanics, Vol. 11, 1976, pp. 59-82.

Supported by the National Science Foundation.

Creep of 304 Stainless Steel under Biaxial Stress

Objective: To investigate the behavior of 304 stainless at elevated temperatures under combined stressing and develop suitable constitutive equations.

Approach: Experiments are employed in which the temperature and state of combined tensions and torsion are altered abruptly according to a planned schedule.

Progress: Apparatus modification required for tests at 1200° have been made and long-time constant stress tests have been performed at 1100°F and effective stresses of 10, 12.5 and 15 ksi. Apparatus for creep in compression and internal pressure in tubes has been developed.

Cyclic creep tests have been performed following creep for 1000 hr. Yield surface subsequent to creep for 1000 hr. has been explored. A model to describe plasticity, creep and recovery is being investigated.

Additional creep experiments have been performed under various combinations of tension and torsion. Recovery and reloading strains have been observed. A creep surface for this material has been compared with experimental data.

Principal Investigator: W. N. Findley (Engineering)

Personnel: R. Mark (Engineering), R. M. Reed (Engineering) and U. W. Cho (Engineering).

Publications: Findley, W. N., and Mark, R., "Multiaxial Creep Behavior of 304 Stainless Steel," Annual Report No. 4 on Union Carbide Subcontract 3599, July 1975.

A manuscript by Mark and Findley has been preapred on the creep surface investigations.

Supported by the Oak Ridge National Laboratory.

Multiaxial Creep and Relaxation of 2618 Aluminum Alloy

Approach: A tubular specimen is subjected to creep in torsion and stress relaxation in tension simultaneously, as well as various step changes in combined tension and torsion creep.

Progress: Experimental work on the aluminum alloy has been completed. Creep and recovery in tension and creep under combined tension and torsion have been analyzed and a constitutive equation to take into account creep and recovery has been characterized.

Creep behavior under step changes in stress and stress reversal have been calculated from a constitutive equation and compared with experiments. A new model is being explored.

Principal Investigator: W. N. Findley (Engineering)

Personnel: J. S. Y. Lai, Associate Professor, School of Civil Engineering, Georgia Institute of Technology.

Publications: None. Manuscript on one phase completed.

No Support.

Approximate Renormalisation Group Transofrmations

Recently Kadanoff, Yalabik and the author have analysed a renormalisation group transofrmation with a variationally determined parameter. The method has been used to study the critical behaviour of spin systems with isotropic short range interactions in the presence of an additional cubic anisotropic interaction. It is found that, at space dimensionality $d = 3$, the isotropic fixed point is unstable against cubic perturbations for order parameter dimensionality $n \gtrsim 2.3$.

Principal Investigator: A. Houghton

Personnel. M. C. Yalabik (Physics)

Publications: Yalabik, M. C. and Houghton, A., "Approximate Renormalisation Group Calculations of Cubic Cross-over", submitted to Phys. Letters.

Supported by the Advanced Research Projects Agency.

Lecturers in the Materials Research Laboratory Program, 1975-76

August 26, 1975

Solid Mechanics Seminar: Division of Engineering, Dr. M. J. Sewell, Reader in Applied Mathematics, Reading University, SOME MECHANICAL EXAMPLES OF CATASTROPHE THEORY.

September 9, 1975

Solid Mechanics Seminar: Division of Engineering, Dr. J. D. Campbell, Reader in Engineering Science, Oxford University, THE INFLUENCE OF STRAIN-RATE HISTORY ON THE SHEAR STRENGTH OF METALS AT LARGE STRAINS.

September 29, 1975

Solid Mechanics Seminar, Division of Engineering, Professor L. B. Freund, BIFURCATION OF A PROPAGATING CRACK IN A BRITTLE SOLID.

October 2, 1975

Solid State Seminar: Physics Department, Dr. J. J. Hauser, Bell Laboratories, AMORPHOUS CARBON.

October 9, 1975

Solid State Seminar: Department of Physics, Dr. J. Pankove, RCA Laboratories, ELECTROLUMINESCENT AND PHOTOCONDUCTIVE PROPERTIES OF GALLIUM NITRIDE.

Geological Sciences Seminar: Professor Stanley Hart, Massachusetts Institute of Technology, BASALT GEOCHEMISTRY AND HETEROGENEOUS MANTLE.

October 16, 1975

Solid Mechanics Seminar: Division of Engineering, Mr. Jürgen Güldenpfennig, Ruhr University, APPLICATION OF A SELF-CONSISTENT POLYCRYSTAL MODEL TO COMBINED PLASTIC WAVE PROPAGATION.

Materials Science Seminar: Solid State Discussion Group, Professor Bill Giessen, Departments of Chemistry and Mechanical Engineering, Northeastern University, SOME STRUCTURAL AND OTHER ASPECTS OF SPLAT-COOLED METASTABLE ALLOY PHASES.

Solid State Seminar: Department of Physics, Dr. Jack Rowe, Bell Laboratories, CHEMISORPTION AND LOCAL PHOTON FIELDS IN PHOTOELECTRON SPECTROSCOPY.

October 24, 1975

Materials Science Seminar: Division of Engineering, Professor Rishi Raj, Department of Materials Science, Cornell University, MODELS FOR INTERFACIAL CAVITATION AT ELEVATED TEMPERATURE.

October 28, 1975

Solid Mechanics Seminar: Division of Applied Mathematics, Professor A. C. Pipkin, FIBER-REINFORCED COMPOSITES.

October 29, 1975

Materials Science Seminar: Fracture Group, Division of Engineering, Dr. C. J. Beevers, Visiting Professor, Brown University, INFLUENCES OF MICROSTRUCTURE AND ENVIRONMENT ON FATIGUE CRACK GROWTH CHARACTERISTICS OF METALS AND ALLOYS.

October 30, 1975

Solid State Seminar: Department of Physics, Professor R. H. Cole, Brown University, KLAUSIUS-MOSSOTTI AND THE INFERNAL FIELD.

November 3, 1975

Solid Mechanics Seminar, Division of Engineering, Professor Donald A. Simons, Brown University, POROUS MEDIA EFFECTS IN THE STABILIZATION OF SPREADING SHEAR FAULTS.

Physics Colloquium: Professor N. Bloembergen, Division of Engineering and Applied Physics, Harvard University, NON-LINEAR SPECTROSCOPY.

November 6, 1975

Theoretical Seminar: Department of Physics, Professor Norman H. Christ, Department of Physics, Columbia University, QUANTUM EXPANSION OF SOLITON SOLUTIONS.

Solid State Seminar: Department of Physics, Professor D. I. Tchernev, Lincoln Laboratories, Massachusetts Institute of Technology, PHOTO-DECOMPOSITION OF WATER ON SEMICONDUCTING SURFACES.

Geological Sciences Seminar: Professor John Suppe, Department of Geological and Geophysical Sciences, Princeton University, SPECULATION ON SURFACE EFFECTS OF PRESENT-DAY MANTLE CONVECTION.

November 10, 1975

Solid Mechanics Seminar: Division of Engineering and Applied Mathematics, Dr. M. F. Kanninen, Battelle Columbus Laboratories, DYNAMIC CRACK PROPAGATION AND ARREST - THEORY AND APPLICATIONS.

November 13, 1975

Solid State Seminar: Department of Physics, Dr. Hajimu Kawamura, Osaka University and the United States-Japan Eminent Scientists Exchange Program, INVESTIGATION OF THE OPTICAL MODE SOFTENING IN LEAD-TIN TELLURIDE.

November 14, 1975

Special Solid State Seminar and Joint Inorganic Glasses Seminar: Department of Physics, Professor H.-J. Güntherodt, Physics Institute, University of Basel, Switzerland, ELECTRONIC STRUCTURE OF TRANSITION METAL ALLOYS IN THE AMORPHOUS AND IN THE LIQUID STATE.

November 17, 1975

Physics Colloquium: Professor E. Montroll, University of Rochester, NONLINEAR OSCILLATORS.

November 17, 1975

Solid Mechanics Seminar: Division of Engineering, Professor Robert Burridge, Courant Institute of Mathematical Sciences, New York University, AN INFLUENCE FUNCTION FOR THE INTENSITY FACTOR IN TENSILE FRACTURE.

November 20, 1975

Solid State Seminar: Department of Physics, Professor A. H. Luther, Harvard University, RECENT DEVELOPMENTS IN THE THEORY OF ONE-DIMENSIONAL ELECTRON GAS.

November 24, 1975

Physics Colloquium: Dr. S. J. Allen, Bell Laboratories, SUPERIONIC CONDUCTIVITY.

November 24, 1975

Solid Mechanics Seminar: Division of Engineering, Professor J. R. Rice, Division of Engineering, Brown University, INTERFACIAL FRACTURE AND THE EMBRITTLEMENT OF SOLIDS BY A MOBILE DISSOLVED SPECIES SUCH AS HYDROGEN.

December 2, 1975

Special Solid State Seminar (jointly with Electrical Sciences Seminar): Dr. J. Slechta, University of East Anglia, England, MCP METHOD --A GENERALIZATION OF THE BLOCK THEOREM FOR DISORDERED SYSTEMS.

December 4, 1975

Solid State Seminar: Department of Physics, Dr. S. H. Wemple, Bell Laboratories, OPTICAL OSCILLATOR STRENGTHS IN SOLIDS, LIQUIDS AND GASES.

Theoretical Seminar: Department of Physics, Professor Leo Kadanoff, Brown University, RENORMALIZATION APPROACH TO GAUGE AND SPIN SYSTEMS.

December 10, 1975

Fracture Group Seminar: Division of Engineering, Robert McMeeking, Brown University, SOME RESULTS ON CRACK TIP BLUNTING.

December 15, 1975

Solid Mechanics Seminar: Division of Engineering and Applied Mathematics, Professor William N. Findley, Division of Engineering, Brown University, A VISCOUS-VISCOELASTIC MODEL FOR CREEP OF METALS UNDER VARIABLE COMBINED STRESSES AT ELEVATED TEMPERATURE.

December 17, 1975

Joint Solid Mechanics - Materials Science Seminar: Professor W. D. Nix, Department of Materials Science, Stanford University, A MODEL FOR INTERGRANULAR CRACK GROWTH UNDER CREEP CONDITIONS.

December 18, 1975

Solid State Seminar: Department of Physics, Professor M. F. Thorpe, Yale University, DISORDERED 1-DIMENSIONAL SYSTEMS.

January 5, 1975

Solid Mechanics Seminar: Division of Engineering and Applied Mathematics, Dr. A. F. Grandt, Jr., Air Force Materials Laboratory, Wright-Patterson Air Force Base, Dayton, Ohio, FRACTURE MECHANICS STUDIES OF FLAWED FASTENER HOLES.

January 6, 1976

Special Solid State Seminar: Department of Physics, [illegible] University, CYCLOTRON [illegible] STUDIES OF [illegible] UNDER INTENSE OPTICAL EXCITATION.

January 8, 1976

Solid State Seminar: Department of Physics, Dr. Koji, Kajimura, IBM, Thomas J. Watson Research Center and Electrotechnical Laboratory, Tokyo, MAGNETOACOUSTIC EFFECTS IN BI SINGLE CRYSTALS.

January 9, 1976

Chemistry Colloquium: Dr. Howard McKinzie, GTE Laboratories, Inc., Waltham, Massachusetts, CATALYSTS FOR INDUSTRIAL POLLUTION CONTROL.

February 2, 1976

Solid Mechanics Seminar: Division of Engineering and Applied Mathematics, Professor John Hutchinson, Division of Engineering and Applied Physics, Harvard University, INELASTIC AND CREEP BEHAVIOR OF POLY-CRYSTALLINE MATERIALS.

February 4, 1976

Fracture Seminar: Division of Engineering, Mr. Lawrence S. Costin, Brown University, A NEW EXPERIMENTAL TECHNIQUE IN DYNAMIC FRACTURE INITIATION.

February 5, 1976

Solid State Seminar: Department of Physics, Professor Elliott W. Montroll, University of Rochester, UNUSUAL TRANSPORT AND STOCHASTIC PROCESSES, ESPECIALLY AS APPLIED TO AMORPHOUS MATERIALS.

February 6, 1976

Chemistry Colloquium: Dr. M. Churchill, State University of New York, STRUCTURAL STUDIES ON TRANSITION METAL HYDRIDES AND HALIDES.

February 9, 1976

Physics Colloquium: Dr. H. D. Hagstrum, Bell Laboratories, STUDIES OF CHEMISORPTION BY TWO DIFFERENT ELECTRON SPECTROSCOPIES.

Solid Mechanics Seminar: Division of Applied Mathematics, Dr. Jean Bataille, Université Claude Bernard and Ecolé Centrale at Lyon, ENERGY EQUATIONS FOR MIXTURES.

February 10, 1976

Informal Solid Mechanics Seminar: Divison of Applied Mathematics, Professor E. H. Lee, Divison of Applied Mechanics, Stanford University, STEADY-STATE METAL FORMING ANALYSES.

February 10, 1976

Solid State Seminar: Department of Physics, Professor Chia-Wei Woo, Department of Physics, Northwestern University, STATISTICAL MECHANICS OF LIQUID CRYSTALS.

February 11, 1976

Special Theoretical Seminar: Department of Physics, Professor H. M. Fried, Brown University and Saclay, France, EIKONAL APPROXIMATIONS IN QUANTUM STATISTICAL MECHANICS.

February 16, 1976

Solid Mechanics Seminar: Divisions of Applied Mathematics and Engineering, Professor E. H. Lee, Division of Applied Mechanics, Stanford Unviersity, ON THE INFLUENCE OF VARIATIONS OF MATERIAL PROPERTIES ON STRESS WAVE PROPAGATION THROUGH ELASTIC SLABS.

February 17, 1976

Nuclear Seminar: Department of Physics, Dr. P. Moffa, Brookhaven National Laboratory, HEAVY ION REACTION STUDIES (Localization; Inelastic Scattering).

February 19, 1976

Solid State Seminar: Department of Physics, Professor Robert G. Wheeler, Department of Enginering and Applied Science, Yale University, SPECTROSCOPY OF SPACE CHARGE LAYERS AND SEMICONDUCTORS.

March 4, 1976

Solid State Seminar: Department of Physics, Dr. Robert C. Dyners, Bell Laboratories, SUPERCONDUCTIVITY IN THE STRONG COUPLING LIMIT.

March 8, 1976

Research Seminar in Pattern Theory: Division of Applied Mathematics, Professor Ulf Grenander, Brown University, SOME PATTERNS IN X-RAY DIFFRACTION.

March 15, 1976

Solid Mechanics Seminar: Division of Engineering, Dr. Edward W. Hart, Department of Theoretical Mechanics and Materials Science, Cornell University, CONSTITUTIVE RELATIONS FOR METAL DEFORMATION.

March 15, 1976

Physics Colloquium: Professor S. Berko, Brandeis University, THE LAMB SHIFT OF THE n = 2 STATE OF POSITRONIUM.

March 17, 1976

Materials Science Seminar: Division of Engineering, Dr. Elaine Savage, U. S. Department of Transportation, THE ROLE OF THE SURFACE IN THE MECHANICAL BEHAVIOR OF TITANIUM.

March 18, 1976

Solid State Seminar: Department of Physics, Professor A. Klein, University of Pennsylvania and M.I.T., SOLICONS AND BOUND STATES IN THE GROSS, NEVEU MODEL.

Solid Mechanics Seminar: Division of Engineering, Professor William Prager, Savnognin, Switzerland, OPTIMIZATION OF STRUCTURAL LAYOUT.

Solid State Seminar: Department of Physics, Dr. D. Emin, Sandia Laboratories, SMALL POLARON FORMATION AND MOTION.

March 19, 1976

Chemistry Colloquium: Professor Arthur Hubbard, University of Hawaii, ELECTROCHEMISTRY OF SINGLE CRYSTALS.

Materials Science Seminar: Division of Engineering, Dr. S. R. Bodner, Visiting Professor, Division of Engineering, Brown University, CONSTITUTIVE EQUATIONS FOR CYCLIC LOADING OF RATE DEPENDENT MATERIALS.

March 22, 1976

Solid Mechanics Seminar: Divisions of Applied Mathematics and Engineering, Professor Alan Needleman, Brown University, THE LEAD BALLOON PROBLEM; NECKING OF INTERNALLY PRESSURIZED SPHERICAL MEMBRANES.

March 23, 1976

Center for Neural Studies Seminar: Division of Applied Mathematics, Professor Ford Ebner, Brown University, SYNAPTIC PLASTICITY.

Experimental Seminar: Department of Physics, Bruce B. Chick, Metals Research Laboratory, Brown University, DESIGN AND CONSTRUCTION OF AN ULTRASONIC INTERFEROMETER.

March 26, 1976

Chemistry Colloquium: Dr. Ralph H. Staley, Massachusetts Institute of Technology, NEW INSIGHTS INTO MOLECULAR BASE STRENGTHS AND CARBONIUM ION STABILITIES USING ION CYCLOTRON RESONANCE SPECTROSCOPY.

March 29, 1976

Solid Mechanics Seminar: Divisions of Applied Mathematics and Engineering, Professor Y. Weitsman, Materials Science Laboratory, Wright-Patterson Air Force Base, A MIXTURE THEORY FOR LONGITUDINAL WAVES IN FIBER-REINFORCED COMPOSITES.

March 30, 1976

Center for Neural Studies Seminar: Division of Applied Mathematics, Professor Ford Ebner, Brown University, SYNAPTIC PLASTICITY.

April 1, 1976

Theoretical Seminar: Professor Carl Bender, Department of Mathematics, M.I.T., STATISTICAL ANALYSIS OF FEYNMAN'S DIAGRAMS.

Geological Sciences Seminar: Dr. Michael Chinnery, Seismological Laboratory, M.I.T., DAMAGING EARTHQUAKE PROBABILITIES AND NUCLEAR POWER PLANT DESIGN-CRITERIA.

April 12, 1976

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Physics Colloquium: Professor L. Spruch, New York University, ATOMS IN INTENSE MAGNETIC FIELDS.

April 13, 1976

Chemistry Colloquium: Dr. Leslie Woodcock, ASPECTS OF LIQUID GLASS TRANSITION PHENOMENA.

April 15, 1976

Solid State Seminar: Department of Physics, Dr. David Penn, National Bureau of Standards, FIELD EMISSION SPECTROSCOPY.

April 16, 1976

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April 21, 1976

Solid State Seminar: Department of Physics, Dr. Bernard Bendow, Air Force Lab, Hanscom, MULTIPHONON ABSORPTION AND SCATTERING IN SEMICONDUCTORS.

Theoretical Seminar: Department of Physics, Professor C. G. Callan, Princeton University, CONFINEMENT IN TWO DIMENSIONAL YANG MILLS THEORIES.

Joint Solid Mechanics Seminar-Materials Science Seminar: Division of Engineering, Professor D. M. Barnett, Department of Materials Science, Stanford University, SELF-FORCES ON SINGULAR DISLOCATIONS.

April 23, 1976

Solid Mechanics Seminar: Divisions of Applied Mathematics and Engineering, Dr. Alan Head, University of Melbourne, DISLOCATIONS OF THE SAN ANDREAS FAULT.

April 26, 1976

Solid Mechanics Seminar: Divisions of Applied Mathematics and Engineering, Dr. V. Vitek, Central Electricity Research Laboratories, Leatherhead, England, PLASTIC DEFORMATION OF BCC METALS AND COMPUTER SIMULATION OF DISLOCATION MOTION.

April 28, 1976

Solid State Seminar: Department of Physics, Dr. Horst Stormer, Bell Laboratories and Max Planch Institute, Grenoble, LUMINESCENCE FROM ELECTRON HOLE DROPS IN GERMANIUM AND IN STRONG MAGNETIC FIELDS.

May 3, 1976

Solid Mechanics Seminar: Divisions of Engineering and Applied Mathematics, Professor R. A. Schapery, Texas A & M University, CRACK PROPAGATION IN VISCOELASTIC MATERIALS.

Physics Colloquium: Dr. C. C. Grimes, Bell Telephone Laboratories, ELECTRONS ON A LIQUID HELIUM SURFACE: A ONE-DIMENSIONAL ATOM AND/OR A TWO-DIMENSIONAL PLASMA.

May 6, 1976

Solid State Seminar: Department of Physics, Dr. L. Passell, Brookhaven National Laboratory, NEUTRON SCATTERING STUDIES OF PHYSISORBED LAYERS.

May 7, 1976

May 10, 1976

Solid Mechanics Seminar: Divisions of Applied Mathematics and Engineering, Professor J. H. Weiner, Division of Engineering, Brown University, POLYMER MECHANICS FROM THE ATOMISTIC VIEWPOINT.

May 11, 1976

Fracture Discussion Group: Division of Engineering, Professor M. F. Ashby, Harvard University, THE DEVELOPMENT OF FRACTURE MECHANISM DIAGRAMS.

May 13, 1976

Solid State Seminar: Department of Physics, Professor S. S. Mitra, University of Rhode Island, MULTIPHONON PROCESSES IN SOLIDS.

May 21, 1976

Chemistry Colloquium: Dr. Lothar Brixner, E. I. DuPont de Nemours, Eu^{+2} FLUORESCENCE IN BARIUM CHLORIDE.

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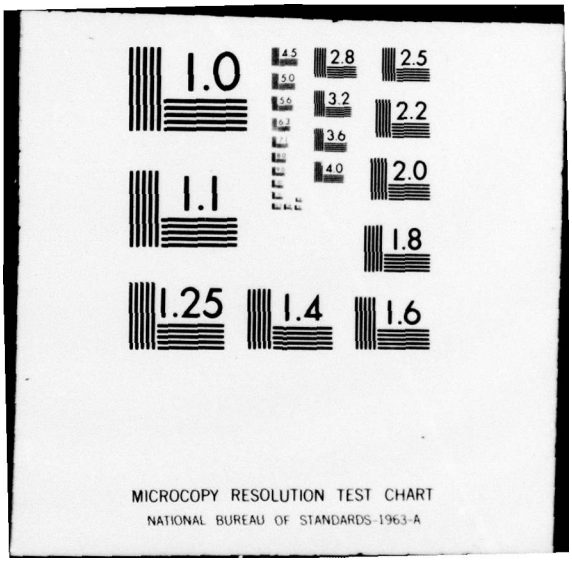
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F. Bucholtz	Fellow
J. Meyer	Fellow
G. Robertshaw	Fellow

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